EFFECT OF CERAMIC NANO FILLERS ON POLYETHYLENE PROPERTIES

BY

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Dedicated To My beloved Parents and Family members

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LIST OF ABBREVIATIONS

HDPE	:	High Density Polyethylene
LDPE	:	Low Density Polyethylene
TGA	:	Thermal Gravimetric Analyzer
DSC	:	Differential Scanning Calorimeter
WAXD	:	Wide Angle X ray Diffraction
MC	:	Micro calorimeter
GPC	:	Gel Permeation Chromatography
SNTP	:	Synthetic tubes like nano-particles
PEEK	:	Polyether ether ketone
THR	:	Total Heat Release
HRC	:	Heat Release Capacity
FSP	:	Flame Spray Pyrolysis

ABSTRACT

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Ethylene Polymerization was done to form Polyethylene nano-composite with Nano-Aluminum Nitride and Nano-Silicon Nitride using zirconocene catalysts. Activity results show that catalyst activity is maximum at 15 mg nano-Ceramic fillers in both cases. Differential Scanning Calorimeter (DSC) results show that percentage crystallanity was also marginally higher at this amount of filler in case of Nano-Aluminum Nitride, However in case of Nano-silicon Nitride crystallanity decreases slightly with increase in amount of filler. Results were also confirmed by performing WAXD (Wide Angle X ray Diffraction). Thermal behavior of polyethylene nano composites (0, 15, 30, and 45) mg was studied by Differential Scanning Calorimeter (DSC) and Thermal Gravimetric Analyzer (TGA). Morphology of the component with 15 mg AlN is more fibrous as compared that with 0 mg AlN and higher filler loading as shown by SEM images. In case of SiN morphology of the component with (15, 30) mg SiN is more fibrous as compared that with control and higher filler loading as shown by SEM images. Micro-calorimeter (MC) results showed decrease in combustibility in polyethylene nano-composites as the filler loading increases. In another part of thesis blending of these nano-fillers were also

done with LDPE (Low Density Polyethylene) and effect on thermal properties was observed with different characterizing equipments like DSC and Micro calorimeter (MC).

ملخص الرسالة

ملخص الرسالة

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لقد تم بلمرة الإثيلين لتشكيل بولي الإثيلين مركب مع نانو نتريد الألمنيوم ونتريد السيليكون باستخدام المواد الحفازة ال zirconocene. النتائج اظهرت ان نشاط الحفازالعظمى كانت باستخدام 15 ملي جرام من حشوات النانو سيراميك في كل الحالات. أظهرت النتائج باستخدام الماسح الحراري التفاضلي (DSC) أن نسبة التبلور(crystallanity) كانت أيضا الاعلى باستخدام نفس هذه الكمية من الحشو في حالة حشوات النانو نتريد الالومنيوم ، ولكن نسبة التبلور(crystallanity) تقل مع زياده كمية حشوات النانو نتريد السيليكون. ولقد تم تاكيد النتائج باستخدام WAXD .ولقد تم دراسة السلوك الحراري لمركب النانوبولي ايثلين (0، 15، 30، و 45) ملي جرام باستخدام الماسح الحراري التفاضلي (DSC) ومحلل الحراري الوزني (TGA). ولقد اظهرت الفحوصات المورفولوجية ان المركب يحتوي على نسبة الياف اعلى في حالة استخدام 15 ملي جرام من مع نانو نتريد الألمنيوم كما يتضح من صور SEM. في حالة نانو نتريد السيليكون فان استخدام (15، 30) ملي جرام يحتوي على نسبة اعلى من الالياف م كما يتضح من صورSEM . وأظهرت Micro-calorimeter (MC) انخفاض في الاحتراق في المركبات النانو بولي ايثيلين كلما كمية الحشو. في جزء آخر من هذه الرسالة اجريت عملية مزج هذه الحشوات النانومتريه مع LDPE (البولي إثيلين منخفض الكثافة) كما لوحظ تأثير على الخواص الحرارية باستخدام DSC و (MC).

CHAPTER 1

INTRODUCTION

Composites having nanometer sized particle dispersed within polymer matrix are called Polymer Nano-Composites, having range of properties and industrial applications [1]. And technology which deals with these types of composites is known as Nanotechnology, [2] [3] where as it's also a science of design, fabrication and application of nano sized structures. No doubt it's a young field and enrichment is still about to come but it is encompassing nearly every discipline of science and engineering. Research is sprouting now a day in terms of publications and practical possibilities [4-7].

From years we are using macro size particles in polymer matrix for the enhancement of properties, at that time length of scale is micrometers and the interface of fillers is close to the bulk polymer matrix [8].In case of nano composites, where the length of scale is nano meter particle has ultra large interfacial area per unit volume [9], and the distances between the polymer and filler components are extremely short. Therefore the molecular interaction between the polymer and nano-particles will give polymer nano composites an extra ordinary property that conventional polymer does not have [10]. Function played by nano particle is compared to particle's chemical composition and its individual property [11]. When we are going to introduce nano particles into polymer system that is already in an inorganic nature, the polymer nano composites will itself exhibit multifunctional, high performance polymer characteristics beyond the conventionally

filled polymeric materials [12-15].The development of these new materials will enable us by revealing its latest properties and un-covering ultimate insight between the materials that will surely come into picture when their instinct morphology and dynamics overlap at nano scales [16-20].

In polymer world commercialized polymer of olefin called polyolefin has a wide range of application because of its different properties. Its demand in the world market depends on the characteristics of polyolefin produced. Polyethylene competes rigorously in a category of wide range of application and its ambitious to say polyethylene accounts for 50% of total polymer demand. Different fillers are already well known to improve the properties of parent polymer both in terms of mechanical and thermal stability. Loyalty of inorganic fillers lies in an increase in thermal conductivity where as organic fillers improve mechanical properties [21].

Different filler are now being used depending on various applications; most commonly used fillers are as that can be seen in most of the literature works [22].

- Montmorillonite organoclays [MMT]
- Carbon nano fibers [CNFs]
- Polyhedral oligomeric silsesquioxane [POSS®]
- Carbon nanotubes [multiwall [MWNTs],small-diameter [SDNTs],and single-wall [SWNTs]]
- Nano-silica [N-silica]
- Nano-aluminum oxide [Al203]

- Nano-titanium oxide [TiO]

Fillers that we are trying to use is Aluminum nitride and Silicon nitride that are already known for providing its best thermal behavior, which is already verified with micro size filler with different method of preparation [23].

1.1 Aluminum Nitride

Aluminum Nitride with formula AlN is a newer material in the groups of ceramics and no doubt its discovery was made some 100 years ago, but its commercially applicability developed in last two decades. Because of controlled and reproducible properties are getting general importance. Some of the major properties of Aluminum Nitride is good thermal conductivity and low thermal expansion coefficient, close to that of Silicon. Non reactive with normal semiconductor process chemicals and gases. Instead of filler its alone use is quite common , for example use of substrates for electronic packages ,heat sinks , IC(integrated circuit) packages ,Power transistor bases , microwave device packages, material processing kiln furniture, semiconductor processing chamber fixtures and insulators, molten metal handling components . Hexagonal structure which is covalently bonded is formed from sintering aids and hot pressing, its nature of being stable at very high temperature range in an inert atmosphere made its utility extra important and surface oxidation occurs at temperature of $700^{o}C$, during the atmosphere of oxygen same the layer of aluminum oxide is formed as we use to say it as corrosion which can protect the material up to temperature of $1350^{o}C$. This material do dissolve in mineral acids, whereas hydrolyze slowly in water, current applications are in electronics

area where the heat removal is very important and serious issue. Literature shows that AlN can be best non-toxic alternative to beryllia, different metallization methods are known to allow the AlN to be in place of alumina and BeO that has further electronic applications. Following is the general data sheet for AlN (aluminum nitride) which includes mechanical, thermal, and electrical properties [24-26].

Table 1 Following table is taken from the reference [27] in order to elaborate the exact property values.

Mechanical	Units of Measure	SI/Metric	(Imperial)
Density	gm/cc (lb/ft^3)	3.26	(203.5)
Porosity	% (%)	0	(0)
Color	—	gray	—
Flexural Strength	MPa (lb/in^{2}x10^3)	320	(46.4)
Elastic Modulus	GPa (lb/in^{2}x10^6)	330	(47.8)
Shear Modulus	GPa (lb/in^{2}x10^6)	—	—
Bulk Modulus	GPa (lb/in^{2}x10^6)	—	—
Poisson's Ratio	—	0.24	(0.24)
Compressive Strength	MPa (lb/in^{2}x10^3)	2100	(304.5)
Hardness	Kg/mm^2	1100	—
Fracture Toughness K_{IC}	MPa•m$^{1/2}$	2.6	—
Maximum Use Temperature (no load)	°C (°F)	—	—
Thermal			
Thermal Conductivity	W/m•°K (BTU•in/ft^2•hr•°F)	140–180	(970–1250)
Coefficient of Thermal Expansion	10^{-6}/°C (10^{-6}/°F)	4.5	(2.5)
Specific Heat	J/Kg•°K (Btu/lb•°F)	740	(0.18)
Electrical			
Dielectric Strength	ac-kv/mm (volts/mil)	17	(425)
Dielectric Constant	@ 1 MHz	9	(9)
Dissipation Factor	@ 1 MHz	0.0003	(0.0003)
Loss Tangent	@ 1 MHz	—	—
Volume Resistivity	ohm•cm	>10^{14}	—

1.2 Silicon Nitride

Our next component is Silicon Nitride, used in order to get enhanced thermal behavior, let us consider its general properties, characteristics and field of application. In the same way as aluminum nitride this type of material is produced through pressing and sintering with advanced methods to produce a material for ceramic. The material has a white grayish to black in color and can be polished to a very smooth reflective surface, giving parts with a striking appearance. High Performance silicon nitride materials were developed for automotive engine wear parts, such as valves. The cost of the ceramic parts never dropped enough to make the ceramics feasible in engines and turbochargers. The very high quality bodies developed from these contains severe high consistency in applications and are available today in many mechanical, thermal and wear applications. Major properties of silicon nitride are high strength over a wide temperature range, high fracture toughness, high hardness and outstanding wear resistance, impingement and frictional modes, good thermal shock resistance, good chemical resistance. silicon nitride because of its aforementioned properties have different field of applications like in rotating bearing balls and rollers cutting tools, engine moving parts, valves, turbocharger rotors. Engines wear parts, turbine blades, vanes, buckets. Metal tube forming rolls and dies, precision shafts and axles in high wear environments. On the next page is the general data sheet for SiN (Silicon nitride) which includes mechanical, thermal, and electrical properties [28-31].

Table 2 Following table is taken from the reference [31] in order to elaborate the exact property values.

Mechanical	SI/Metric (Imperial)	SI/Metric	(Imperial)
Density	gm/cc (lb/ft^3)	3.29	(205.4)
Porosity	% (%)	0	(0)
Color	—	black	—
Flexural Strength	MPa ($lb/in^2 x10^3$)	830	(120.4)
Elastic Modulus	GPa ($lb/in^2 x10^6$)	310	(45)
Shear Modulus	GPa ($lb/in^2 x10^6$)	—	—
Bulk Modulus	GPa ($lb/in^2 x10^6$)	—	—
Poisson's Ratio	—	0.27	(0.27)
Compressive Strength	MPa ($lb/in^2 x10^3$)	—	—
Hardness	Kg/mm^2	1580	—
Fracture Toughness K_{IC}	$MPa \cdot m^{1/2}$	6.1	—
Maximum Use Temperature (no load)	°C (°F)	1000	(1830)
Thermal			
Thermal Conductivity	W/m•°K (BTU•in/ft^2•hr•°F)	30	(208)
Coefficient of Thermal Expansion	10^{-6}/°C (10^{-6}/°F)	3.3	(1.8)
Specific Heat	J/Kg•°K (Btu/lb•°F)	—	—
Electrical			
Dielectric Strength	ac-kv/mm (volts/mil)	—	—
Dielectric Constant	—	—	—
Dissipation Factor	—	—	—
Loss Tangent	—	—	—
Volume Resistivity	ohm•cm	—	—

CHAPTER 2

LITERATURE REVIEW

David J. Chaiko (known chemist, and had done MS and PhD in Mineral Processing) prepared HDPE nano-composites via melt mixing with 0.3wt% clay; concentration film clarity was drastically increased without affecting the polymer crystallanity, in this invention clay/polymer nano-composites were formed actually by combining an organophilic clay and the polymer, peak re-crystallization temperature of each of the polymer and clay sufficient matches that nano-composite formed has less permeability to gas than polymer [32].

Enhancement of property not only restricted to improve mechanical properties but also in recent work (2011) by Paula.A.Zapata (Process Engineer), polyethylene nano-composite containing silver nano particles with anti microbial properties were produced via in-situ polymerization. In that study it was shown that various silver ion were released through silver nano-composites and have great antimicrobial efficacy against Escherichia coli (Gram-negative, rod-shaped bacterium) [33].

In one of the publication SiO_2/rac-Me_2Si (2-Me-4-Naph-Ind) $2ZrCl_2$ was prepared and different co-catalysts were used, method of preparation was bulk polymerization of propene and co-catalysts were metallocene catalyst. Study also illustrated that

morphology of polymer form can be restricted by altering the co-catalysts. Results suggested that isotactic polypropene have good morphology and high bulk density [34].

Polyolefins is prepared by suspension polymerization with the use of solid titanium catalysts, organ metallic compound (method of preparation) was followed actually through homo-polymerization propylene or copolymerization propylene, Titanium used in the study was prepared by tetravalent titanium compound [35].

Another method of polyolefins production is by suspension polymerization, where as organo aluminum oxy compounds are used as supports. Most importantly in previous literature, Novel Ziegler type catalysts composed of zirconium compounds and organo aluminium oxy compounds had been developed as catalysts for the preparation of ethylene copolymers and that indeed provided high polymerization activity [36].

Another method of preparation is inflation molding, it is actually an invention mostly related to a unique method of preparation which increased the productivity without affecting the 'number average molecular weight', that was verified through gel permeation chromatography (GPC) [37].

2.1 Aluminum Nitride and Silicon Nitride

Aluminum Nitride (AlN) is inorganic filler and it had been used in the improvement of thermal properties. Previously thermal conductivity and stability was determined using nano-sized aluminum nitride (nano-AlN)/cyclo-aliphatic epoxy/trimethaacrylate (TMPTMA).From the studies it appeared that increase in glass transition temperature (T_g)

improved heat resistance where shortest pre-cure time was got through silane treatment [38]. Similarly for silicon nitride (SiN) crystallization behavior of iso-tactic polypropylene was discussed ,SiN was used as filler and crystallization behavior was noted and it's interesting to note that 2 wt% nano-SiN increased the nucleation process and 5 wt% favored crystallite growth [39]. In another study, micro-size (≤10μm) AlN (high performance) was used along with Polyether Ether Ketone (PEEK) by the technique of solution blending. This result approved that AlN particles are very good nucleating agent in addition to that, melting temperature (Tm) increased by 11^{o}C (334^{o}C PEEK control to 345^{o}C) Aluminum Nitride/ Polyether ether ketone (AlN/PEEK) (50/50) and reason illustrated as the perfection of crystallanity was because of enhanced crystal nucleation in region surrounding reinforced particles[40].Again micro-sized [≤10μm]. AlN were used with polystyrene and preparation was done in an ordinary way of mixing the two components at room temperature and mixture was put in stainless steel die, along with hot pressing at 180^{o}C with 45 N Force. Results illustrated the same idea of improving the thermal conductivity with the statement of 20 wt % AlN in pure polystyrene increases five times the thermal conductivity of pure polystyrene [41].

Novel fiber reinforced PE composites were added with SiN particles for enhancing thermal properties, in the same way as it was done with AlN. Moreover method of preparation was same like that of melt mixing, in this study myth of particle size was discussed; by lowering the particle size in a blend improve the thermal conductivity. If we try to make a comparison of AlN and SiN; adding 0-20 % Si_3N_4 filler particles improve the conductivity 5 times and 0-30% AlN fraction improve it by three times[42].

2.2 Metallocene Catalysts

Since our main focus is to improve the activity of the metallocene catalysts and no doubt improvement in thermal properties will be added advantage that already exist in nature of inorganic fillers.

Marcelo P.Gil (Portuguese Scientist) used active supported catalytic system and it was found that co-catalyst methyl aluminumoxane (MAO) activated the mechanism more dramatically than trimethylaluminium (TMA) [43].The metallocene catalysts have been increasing significantly since the 1980's when methylaluminoxane (MAO) was used as co-catalyst for the first time [44].Report also illustrates that at 30 ^{o}C and 60 ^{o}C activity remains the same where as at 90 ^{o}C it lowers down. This study also revealed an interesting fact of catalyst morphology and that is spherical morphology of supported catalyst is replicated in polyethylene particles [45].

The literature shows that metallocene catalysts for olefin polymerization provide very good control on polymerization behavior, structure as well as final polymer properties [46-48].

Metallocene catalysts provide certain flexibility and domain to play with its activity as in comparison to Ziegler Natta catalysts. This is possible by addition of fillers which acts as promoter to catalyst. In past study polyethylene (PE) was synthesized using these metallocene [49] catalysts with the support of zeolite where methyl aluminoxane (MAO) was used as co-catalyst [50]. Evaluation of the study showed that catalyst system without support provided lower activity as compared to the same catalysts when used with the support of zeolite [51]. Ziegler Natta catalysts are no doubt robust but are no longer

capable of winning the race with metallocene catalysts which provide improved activity which means higher yield and higher molecular weight polyolefins. So therefore Polyethylene, Polypropylene and co-polymers are currently produced industrially by metallocene catalysts but still on a relatively small scale. Several problems still exists as difficulty in controlling polymer morphology with soluble catalysts and large amount of MAO needed to achieve maximum catalytic activity [52].

Therefore based on the commercial interest of using metallocene catalysts for olefin polymerization, researchers have put an extraordinary effort for using these metallocene catalysts efficiently [53-56].

Silica balls were also used (of dia. 200-250 nm) as a promoter to metallocene/MAO catalyst. Highest activity was noted at 60^{o}C with 3000 Kgpp/molZr.h.molp/l. [57].Another study also depicted that insitu-polymerization gives a better filler dispersion especially at higher filler content than simple melt compounding. Internal phenomenon that would likely to occur would be that the catalyst absorbed on the surface of filler leads to polymer growth directly on its surface. Other studies also showed that metallocene catalyst supported with alumina-silica exhibited more catalytic activity [58].

Catalytic activities of the metallocene catalysts are already being improved by using mesoporous silica (SBA-15); contribution of this type of addition not only increased the activity but also retain the molecular weight distribution. The work relates and improves on the idea from the previous literature that structurally ordered porous material can act as a better support for heterogeneous catalysts which gives better yields than amorphous porous materials. So it can also be said that higher activity comes from greater strength

that's why our work is projecting the same link which means that AlN can act as a good promoters for catalytic activity. Since no doubt literature reveals an effective way of increasing the activity but on the other hand they are not cost-effective and hence will not benefit industrial economics [59].

Synthetic tubes like nano-particles (SNTP) were used to support metallocene catalysts for ethylene polymerization. One of the major advantages of metallocene catalysts is that molecular structure can be modeled while keeping high catalytic activity. Amorphous and porous silica nano particles have been used as a support for metallocene/MAO catalytic systems in ethylene and propylene polymerization, the reason for using these particles is that they provide better surface area and stability during process but during ethylene polymerization activity was lower so the usage of silica nano-particles provided a better option [60].

Linear Low Density Polyethylene/alumina nano-composites were synthesized by in-situ polymerization with zirconocene/d M-MMAO catalysts, in order to get uniform molecular weight distribution and chemical composition distribution. It could be prepared by co-polymerization of ethylene and high olefin but with the drawback of week mechanical strength [61].

Polyethylene-nano silica (SiO_2) and polyethylene- nano zirconia (ZrO_2) was synthesized via in-situ polymerization with zirconocene MAO catalysts. They reported a five-fold increase in productivity. But the thinking lies in a fact that no-doubt increase in productivity of five times is an achievement but its complexity and expensive nature is present in this study too. For example nano-ZrO_2 filler was synthesized by the flame

spray pyrolysis (FSP) [62] in addition to that they need to get filler-impregnated MAO that must be impurity free. [63-65].

Advantage of using nano-silica and clay particles for ethylene polymerization stems from the idea that particle used as support for metallocene/MAO catalysts remain dispersed in polymer matrix and therefore act as a filler producing polymer-nano composites, but why don't we use a filler that can increase the activity and also will form a nano-composite instead of casting a certain catalysts which have support because this actually increase cost and complexity.

So using of certain filler like AlN-nano & SiN-nano particles that can increase the activity of metallocene catalysts will be a great achievement. Moreover this is an exact combination that provided us with excellent results. The catalytic activity, yield and the particle growth have been studied and optimization has been done. It is fair enough to say that this combination has been used first time in the production of polyolefin, moreover because of its advantages it can be used both in academia and industrial sectors.

2.3 Micro-Calorimeter

Polymers have defined their various applications and replaced materials like metals and woods and that's why we have named this age 'plastic age'. Hot topic of research these days is to determine flammability of particular polymer.

Scientist has provided us with an idea that flammability can become a characteristic of certain polymer, if we incorporate certain substances that can provide this feature [66].

In 2003 Lyon et al. provided a successful idea based on the use of Micro-scale Combustion Calorimeter (MCC).

This type of calorimeter allows us to measure heat release rate, sample size of approx (1-5) mg is pyrolyzed in nitrogen atmosphere with its certain flow rate and 1 K/sec probably is the heating rate. Temperature of 900 ^{o}C is trend to achieve in the presence of oxygen. In that study heat release was calculated through Hugget's Relation; 1 kg of consummated oxygen equals to 13 MJoules of energy release.

Total Heat Release and Heat Release Capacity are the main measured thermal properties [67].HRC is equal to the peak heat release rate (pHRR) divided by the heating rate. Char content can be known by weighing the sample before and after the pyrolysis and heat of combustion (h_c) was calculated according to the relation

$$THR=hc*[100-\%char]/100 \qquad (2.1)$$

Micro-calorimeter that is used in this study is FTT micro calorimeter that was made with the cooperation of Federal Aviation Administration (FAA) it helps us in determining thermo-chemical data in seconds and determines the fire properties of materials.

The technique that is employed in this machine helps us to find of Specific Heat release rate (W/g), Heat of Combustion (J/g) and ignition temperature. Specimen size can be small up to 1 (mg), reliability can be up to +/-5%

Lets view how this technique works in depth, FTT micro-calorimeter uses the same oxygen depletion calorimeter. Sample is heated at constant temperature rise (typically 1 C/s) in a pyrolysis and the product that remained, moved towards pyrolyzer by nitrogen

gas. Gas stream is mixed with O_2 and raised to a temperature of 900 ^{o}C where the decomposition products are oxidized completely.

Oxygen depletion is determined through amount of oxygen and flow rate of combustion gases, where HRR is determined through measurement.

Figure 1 Micro Calorimeter Image

CHAPTER 3

EFFECT OF ALUMINIUM NITRIDE (ALN) ON THE PROPERTIES OF POLYETHYLENE

In the world of thermoplastic polyolefins find wide range of application because of its unique properties such as low cost, light weight, high strength, non-biodegradability, durability, non corrosive nature, and ease in process ability .Among the polyolefins, polyethylene is widely used for variety of applications.

In regard to catalyst activity in polymerization of ethylene, metallocene catalysts provide more flexibility than Ziegler-Natta catalysts. In earlier studies polyethylene (PE) was synthesized using metallocene catalysts [1] with the support of zeolite, wherein methyl aluminoxane (MAO) was used then as co-catalyst [2]. Polyethylene, polypropylene and its co-polymers are currently produced industrially by metallocene catalysts but still on a relatively small scale. Problems still exists as difficulty in regard to control polymer morphology with soluble catalysts and large amount of MAO needed to achieve maximum catalytic activity [4]. There are reports on attempts to use metallocene catalysts for industrial purposes [5-8].

Several studies have been made to improve the various properties of polyethylene by the addition of organic and inorganic fillers [9-12]. However, among these fillers, inorganic fillers increase the thermal properties of the polyethylene significantly [13-15]. In the last two decades, among various inorganic nano-fillers, aluminum nitride (AlN) is of special interest due to its unique thermal properties [16, 17]. Earlier Yu et al. [18] studied the thermal conductivity and thermal stability of the nano-AlN filled cyclo-aliphatic epoxy/trimethaacrylate. The effect of micro-sized (≤10μm) AlN on the properties of polyether ether ketone (PEEK) prepared by solution blending was studied by Boey et al. [19] who reported that AlN can acts as a good nucleating agent in the crystallanity of the polymer. Incorporation of AlN having (≤10μm) in polystyrene also increased the thermal conductivity and maximum was obtained for the composites having 20 wt. % filler [20].

Organic polymers are combustible and flame retardants are used to suppress the combustible process [21-22]. The present reports the result of studies on the properties of polyethylene nano-composites prepared by using metallocene catalysts in presence of aluminum nitride.

3.1 Experiments

3.1.1 Material

Aluminum Nitride (AlN) having size less than 100 nm, zirconocene (catalyst), Toluene and co-catalyst MAO (methylaluminoxane) were purchased from Aldrich Chemicals and

kept in oxygen free environment to avoid any contamination. Ethylene was available in the reactor form cylinder.

3.1.2 Preparation

Polymerization of ethylene was performed in a 250 ml round-bottom flask equipped with a magnetic stirrer. The zirconocene catalyst (6 mg) and required amount of nano-AlN (0, 15, 30 and 45) mg were added to the flask. The reactor was charged with toluene coming from purification chamber so that any of the contamination might not affect the catalysts and co-catalyst. MAO (methylaluminoxane) (5 ml) was used as co-catalysts. The whole process was performed inside a glove box. The reactor was then immersed in a constant temperature bath previously set to desired temperature (30^{o}C, 60^{o}C). After ensuring that bath temperature and reactor temperature was the same, ethylene was introduced into the reactor through an external chamber after removing nitrogen gas under vacuum. Polymerization was quenched after 30 minutes by adding methanol. The polymer was washed with an excess amount of methanol and dried in an oven at 50^{o}C. The conditions used for these present study is given in Table 1.

3.2 Characterization

3.2.1 Activity

Activity of the catalysts is measured by weighing the product and activity was noted as ratio of amount of product (Polyethylene nanocomposite) to amount of catalyst consumed.

3.2.2 Differential Scanning Calorimeter (DSC)

The melting and crystallization behavior of the composites were determined by using DSC-Q1000 (TA instruments). To overcome the thermal history, heating and cooling was done for both first and second cycle's nitrogen atmosphere at the rate of 10°C/min and 5°C/min respectively from a temperature of -10°C to 200°C and third cycle was performed at a rate of 10°C/min and is analyzed in this study.

3.2.3 X-Ray Diffraction (XRD)

Diffractions patterns were obtained through (Rigaku Ultima IV) and crystallanity was determined [23].

3.2.4 Thermo-Gravimetric Analysis (TGA)

Thermal degradation studies were performed by thermo gravimetric measurements using TGA- Q500 (TA instruments). Samples weighing approximately 5 mg were heated in nitrogen atmosphere (purge gas flow: 50 mL/min) from 25° to 650°C at a heating rate of 10°C/min.

3.2.5 Scattering Electron Microscopy (SEM)

The Polymer surface was gold coated and then surface morphology was studied by using Scanning Electron Microscopy (LYRA3GM, TESCAN).

3.2.6 Micro-Calorimeter (MC)

Heat release rate and ignition temperature was determined by using micro-calorimeter (FAA Micro-calorimeter) and sample size varied from 3-4 mg.

3.3 Result and Discussion

3.3.1 Activity

Figure 1 represents the variation in the activity of synthesized polyethylene under various experimental conditions. It was found that the activity of polymerization reaction was higher for the composites having 15 mg of nano-filler (entry no 2) which were prepared using 5 ml of co-catalyst at 30°C. However, further increase in filler content does not improve the activity of polymerization compared to the control (entry no 3 and 4).This observation is similar to that observed earlier in case of Mn doped –titania on the activity of metallocene catalyst by in-situ ethylene polymerization [24]. In order to verify the influence of temperature on activity, reaction was conducted at 60^{o}C (entry no 5 and 6). It is clear from the figure that at high temperature (60^{o}C) activity of reaction increased (entry no 6) when compared to control (entry no 5) but lower than the activity obtained for the reaction at 30^{o}C. (Table 1). Reduction in the amount of co-catalyst also increased the activity of the reaction and was higher for the composites having 15 wt. % of nano-filler (entry no 7 and 8). Results of activity studies are in agreement with the results of DSC and TGA studies.

3.3.2 Differential Scanning Calorimeter (DSC) and X-ray Diffraction (XRD)

Figures 2 display the DSC thermo grams (heating curve) of polyethylene composites as a function of the amount of AlN. The ΔH_{fus}, and Tm values along with the percentage of crystallanity for the blends as a function of AlN content is summarized in Table 2. It can be seen that as the amount of nano-AlN increases, Tm value shifts slightly towards the lower temperature. This can be attributed to the reduction in the lamellar thickness of

crystallites imparted by the presence of AlN in the matrix as observed earlier in case of AlN reinforced HDPE composites [28-30]. The percentage of crystallanity was calculated using the following expression is shown in table 2.

$$\% \text{ of crystallanity} = (\Delta H_{fus}/\Delta H_{0fus}) \times 100 \quad (2)$$

Where ΔH_{fus} is the enthalpy of fusion of the polyethylene composites and ΔH^0_{fus} is the enthalpy of fusion of the 100% crystalline polyethylene. ΔH^0_{fus} of polyethylene was taken as 293 J/g [28]. Incorporation of 15mg of AlN increased the percentage of crystallanity of the polyethylene, and at higher filler loading it shows a deceasing trend. This increase is attributed to the heterogeneous nature imparted by the nano-filler, which results in an increase in the crystallanity of the composites [29]. An increase in the crystal nucleation in the region surrounding the reinforced particles also attributes to increase in the crystallanity of the composites [30]. However, at higher filler loading agglomeration of the nano-filler may occur and a reduction in the mobility of the polymer chains with consequent decrease in the crystallite size and hence a reduction on the percentage of crystallanity [30-32].

Crystallanity is determined through x-ray diffraction (Rigaku Ultima IV), and it showed the same trend as from DSC results as shown by figure 2 (b) [23, 33]. The imperfection of crystals in the presence of the AlN in homogeneities can also contribute to the decrease in crystallanity [34]. This observation has been corroborated with the results TGA analysis.

3.3.3 Thermal Gravimetric Analysis (TGA)

Figures 3 and 4 display the TG and DTG curves for PE composites as a function of the amount of filler. From the TG curves it is clear that degradation kinetics starts at a temperature of 300 ^{o}C and maximum degradation occurred in the range of 425 to 450 ^{o}C and there is no significant variation in the maximum degradation temperature of the composites. However, from the figures 3 and 4, it is clear that addition of 15mg of AlN in the polyethylene matrix increases the thermal stability of the composites while a decrease at higher filler loading. The thermal stability follows the order PE/15 mg AlN <PE < PE/30 mg AlN < PE/45 mg AlN. This can be explained as follows: In the case of composites having 15 mg of AlN, due to its good dispersion in the polymer matrix, dissipation of heat between filler and the matrix occurs efficiently thereby there is an increase in the thermal stability of the composites. Also the low heat capacity of AlN (0.738 J/g/°C) compared to HDPE (1.8 J/g/C) causes to absorb heat rapidly which results in the degradation of polyethylene at higher temperature [27]. Even though, at higher filler concentration, inter-particle distance between fillers decreases, thereby agglomeration and reduction in interfacial area between AlN and PE matrix occurs, this results in the lowering of the thermal stability of the composites. The same trend has been observed by Goyal et al. in the AlN reinforced PEEK composites [37]. The degradation kinetics of the composites can be calculated by using Broido method [34]. based on the assumption that the degradation follows a first order reaction or a superposition of first order process. This assumption of Broido leads to:

$$\ln[-\ln(1-\alpha)] = \ln \mathrm{K} - \frac{\Delta E}{RT} \tag{3}$$

where α the amount of polymer degraded at time t**,** ΔE is the change in activation energy, R is the universal gas constant and T is the temperature in Kelvin scale and K is apparent activation energy. In this, α can be calculated using the following equation:

$$\alpha = \frac{W_o - W_t}{W_0 - W_\infty} \tag{4}$$

Where W_t is the mass at time t, W_o is the initial mass and W_∞ is the mass after infinite time. The advantage of Broido's method of calculating the activation energy of thermal stability is that the result does not depend upon the value of heating rate and is independent of the value of temperature at which the reaction is maximum. The results obtained by using Broido's method for the AlN/Polyethylene composites are given in Figure 4. It can be seen that composites having 15 mg of AlN shows maximum activation energy as compared to other compositions.

3.3.4 Micro-Calorimeter (MC)

Combustibility test data as obtained through Micro Calorimeter in terms of heat release rate and decomposition temperature are shown in Table 3, it is apparent that with increase in the content of filler, heat release rate decreases indicating an increasing in thermal stability and decrease in combustibility [22].

3.3.5 Scanning Electron Microscopy (SEM)

Fig (6a-6d) shows surface morphology, HDPE appears to be less fibrous (see fig 6a) than HDPE/15 mg AlN (see fig 6b).Here fibrous chains are formed making the material more crystalline. In the case of PE/30 mg AlN (see fig 6c), it appears that excess amount of AlN-nano particles restricted the growth of chains and the structure is less fibrous. In

PE/45 mg AlN fibrous surfaces became least prominent (see fig 6d). Scanning Electron Microscopy (SEM) provided us an advantage of exploring the surface morphology of PE (pure) and PE/AlN composites in a better way and same type of effect is also observed in previous studies [38-39].

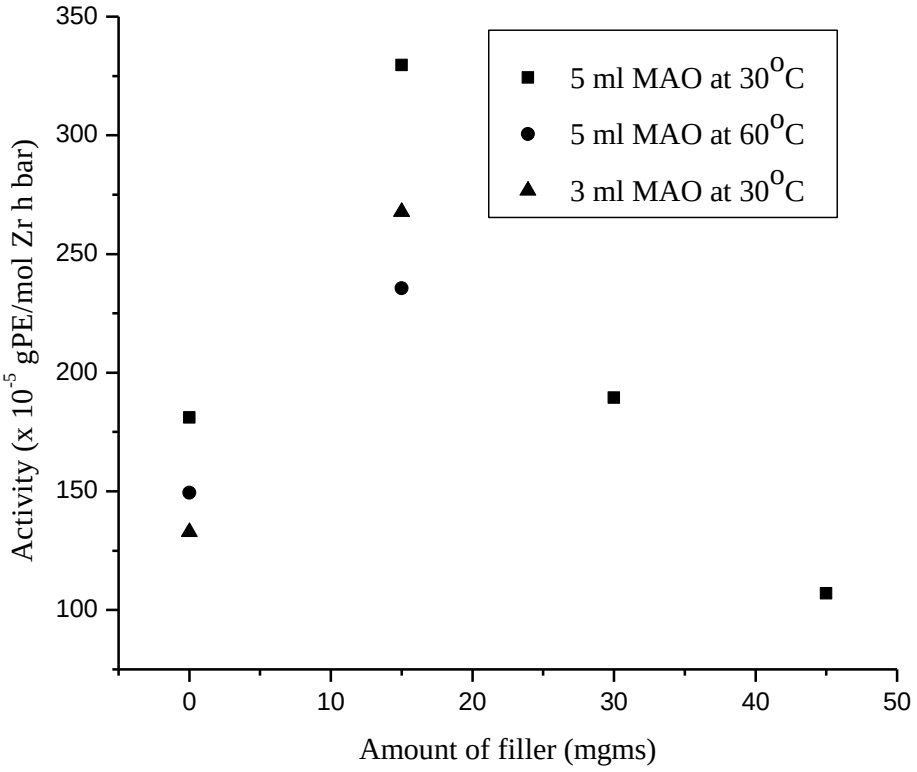

Figure 2 Activity of synthesized polyethylene nanocomposites at different experimental conditions

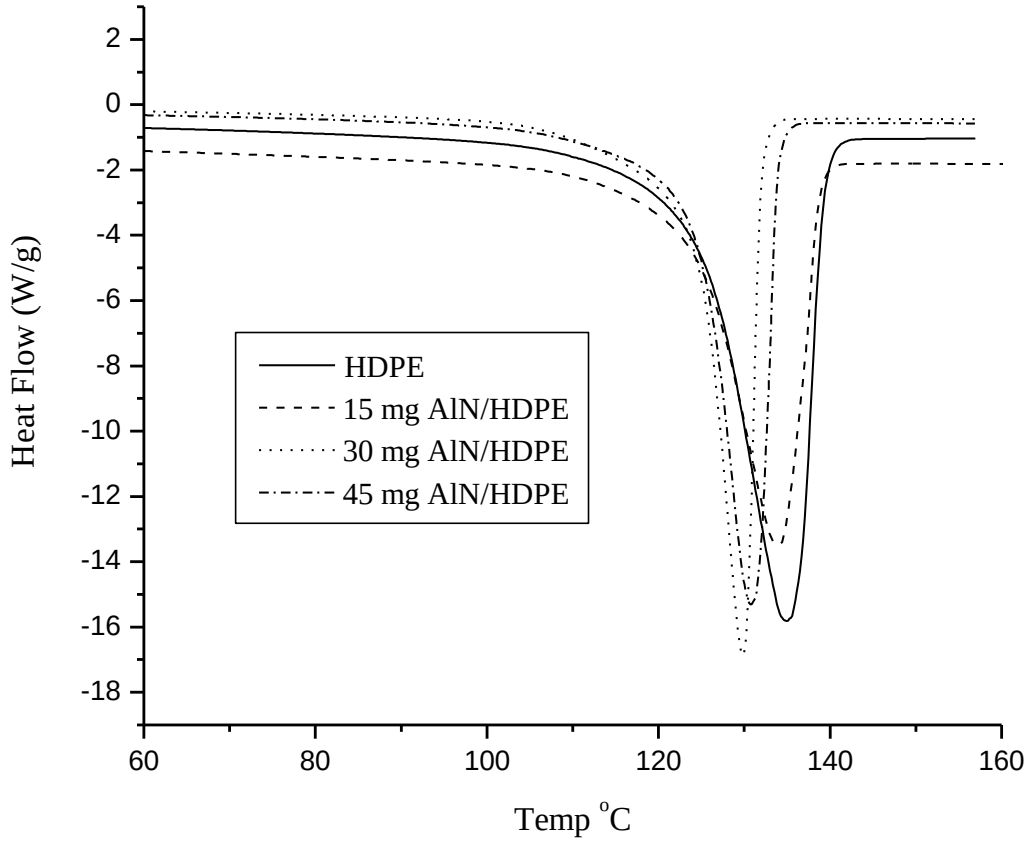

Figure 3 DSC heating curves of nano-AlN filled polyethylene composites

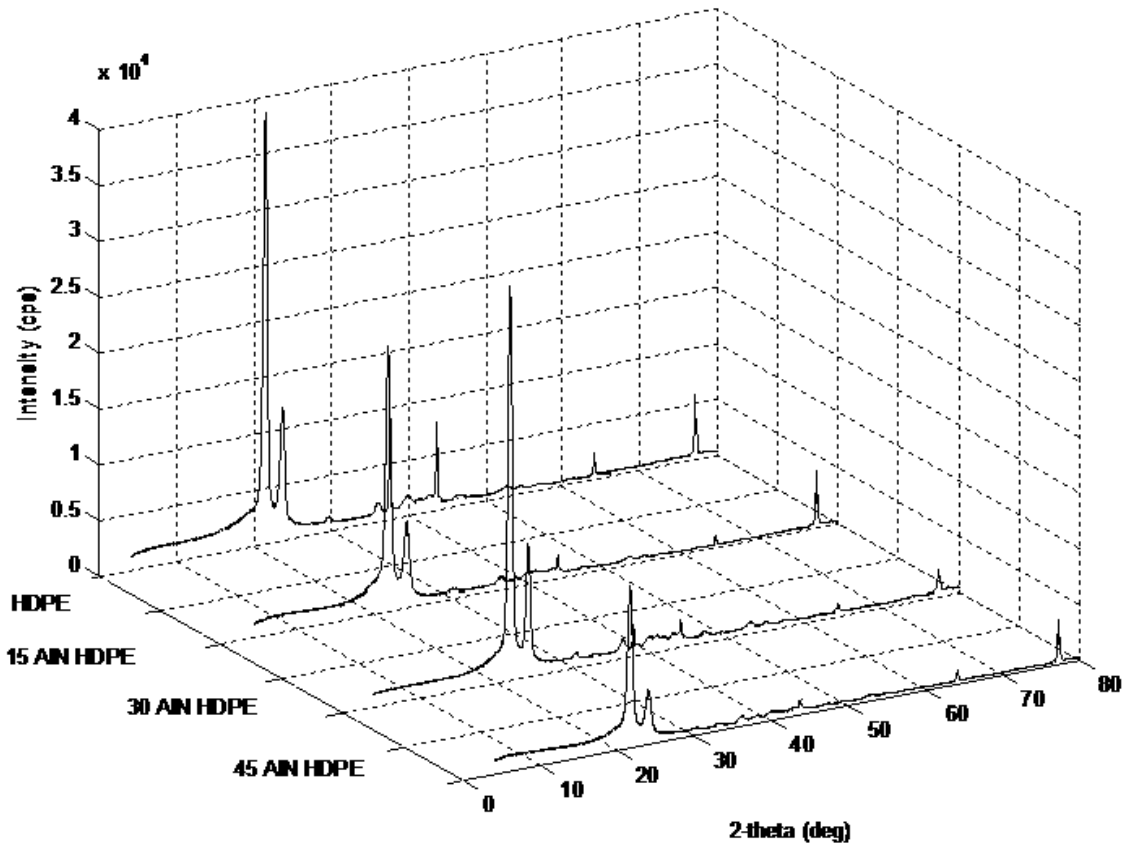

Figure 4 Xray Diffraction (XRD)-intensity vs 2-theta (deg)

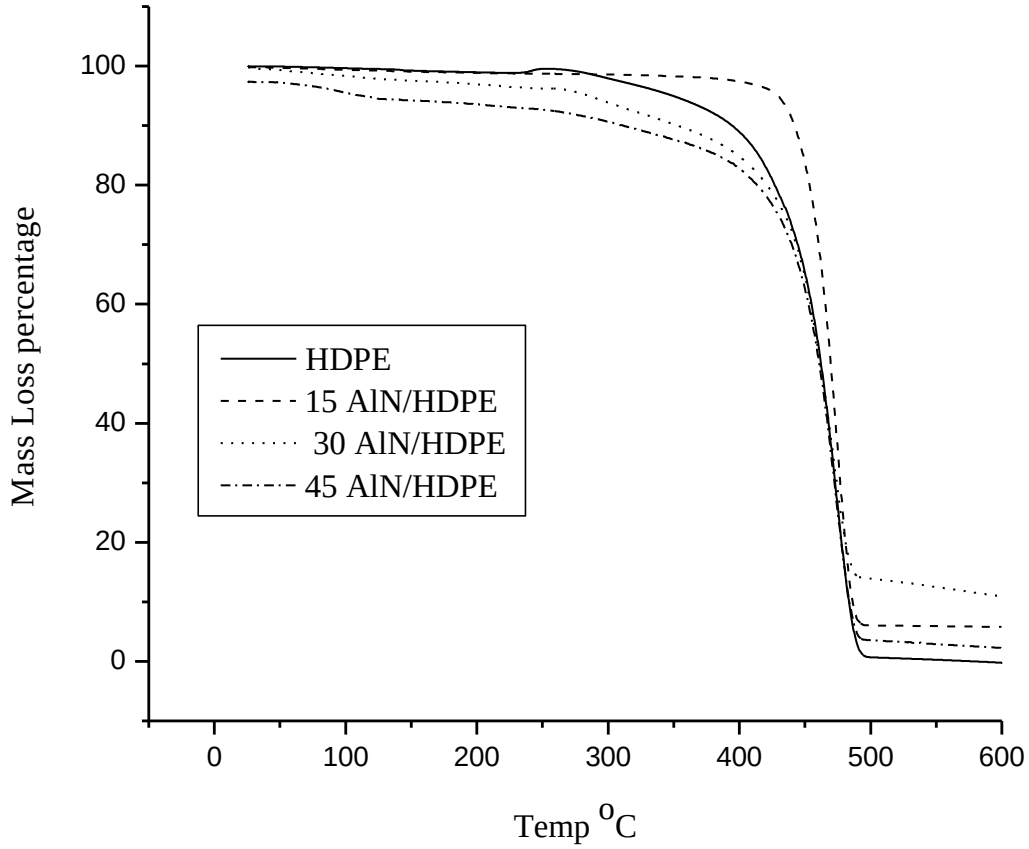

Figure 5 TG plots of nano-AlN filled polyethylene composites

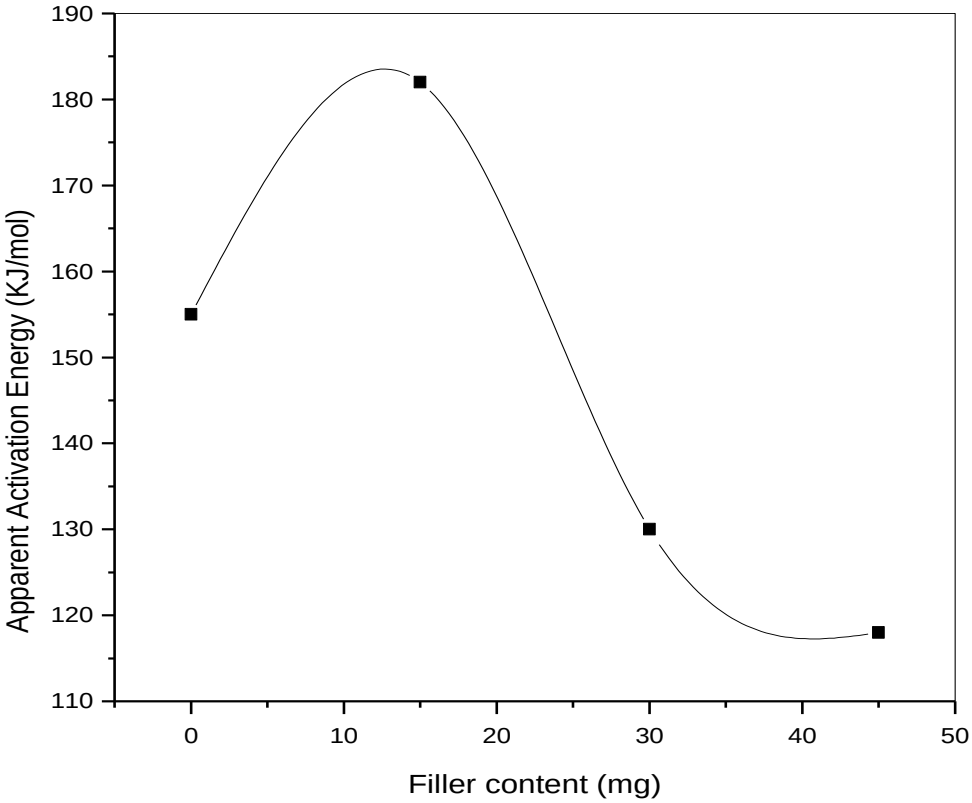

Figure 6 Change in activation energy for the AlN/Polyethylene composites

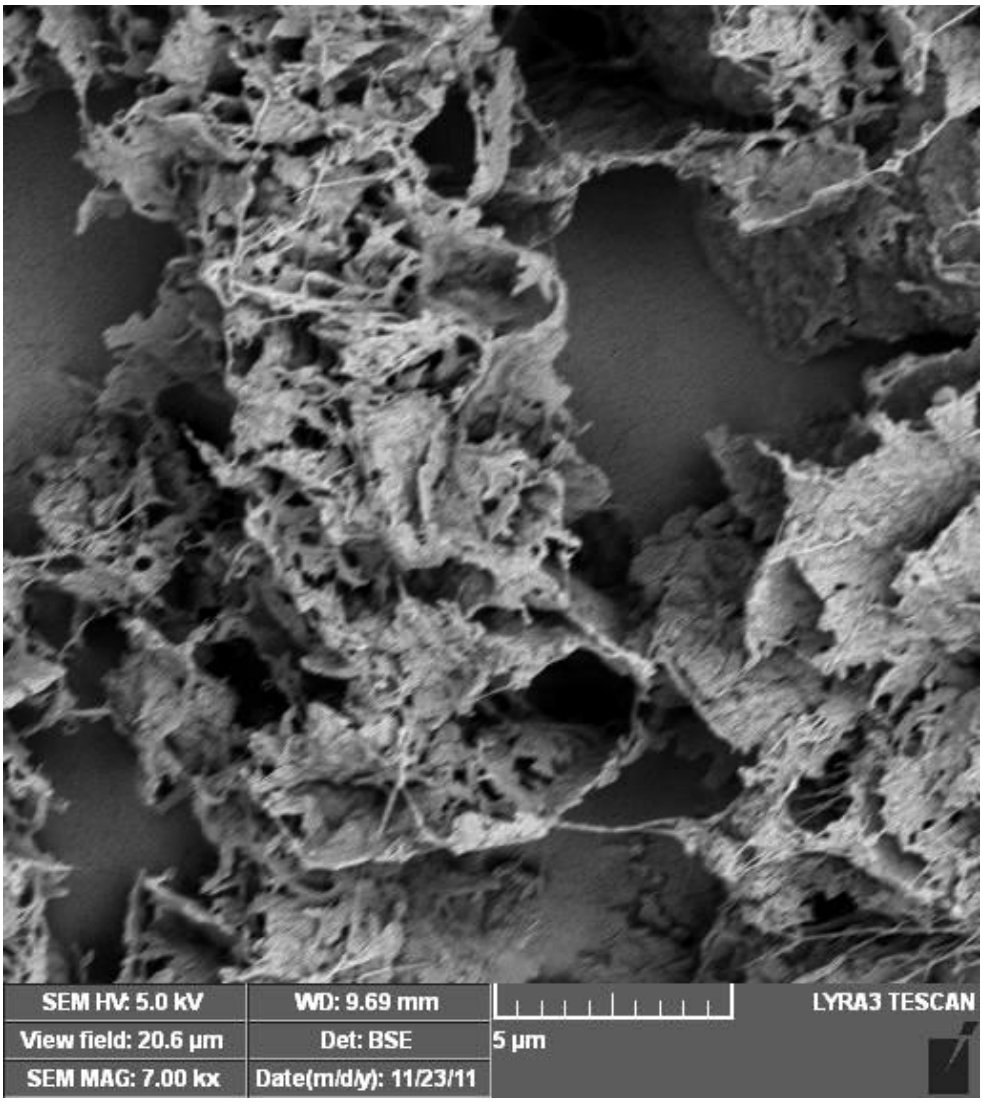

Figure 7 (A-D): Scanning Electron microscopy of nano-AlN filled polyethylene composites A-Pure HDPE

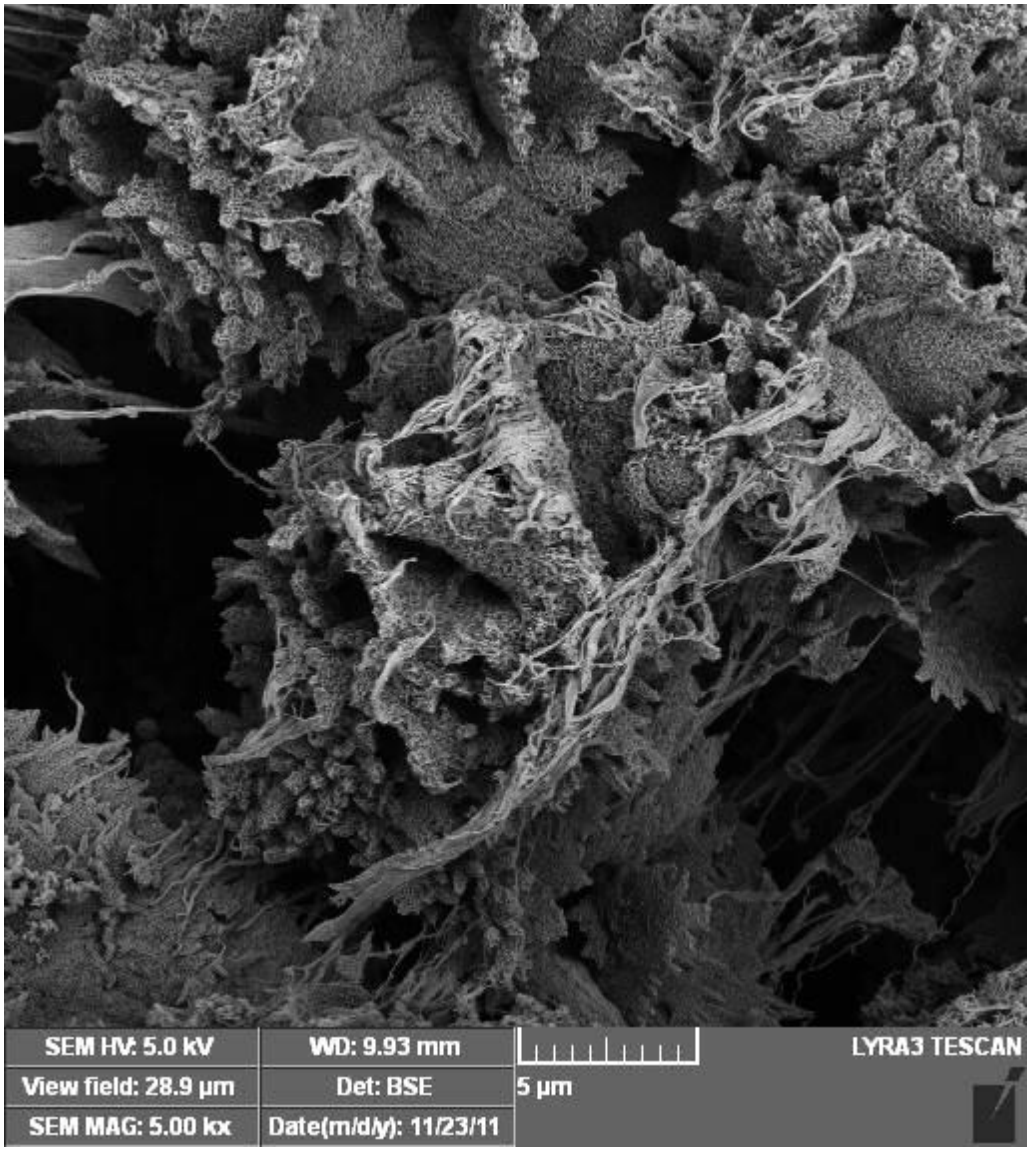

Figure 8 (A-D): Scanning Electron microscopy of nano-AlN filled polyethylene composites B-15mg AlN/ HDPE

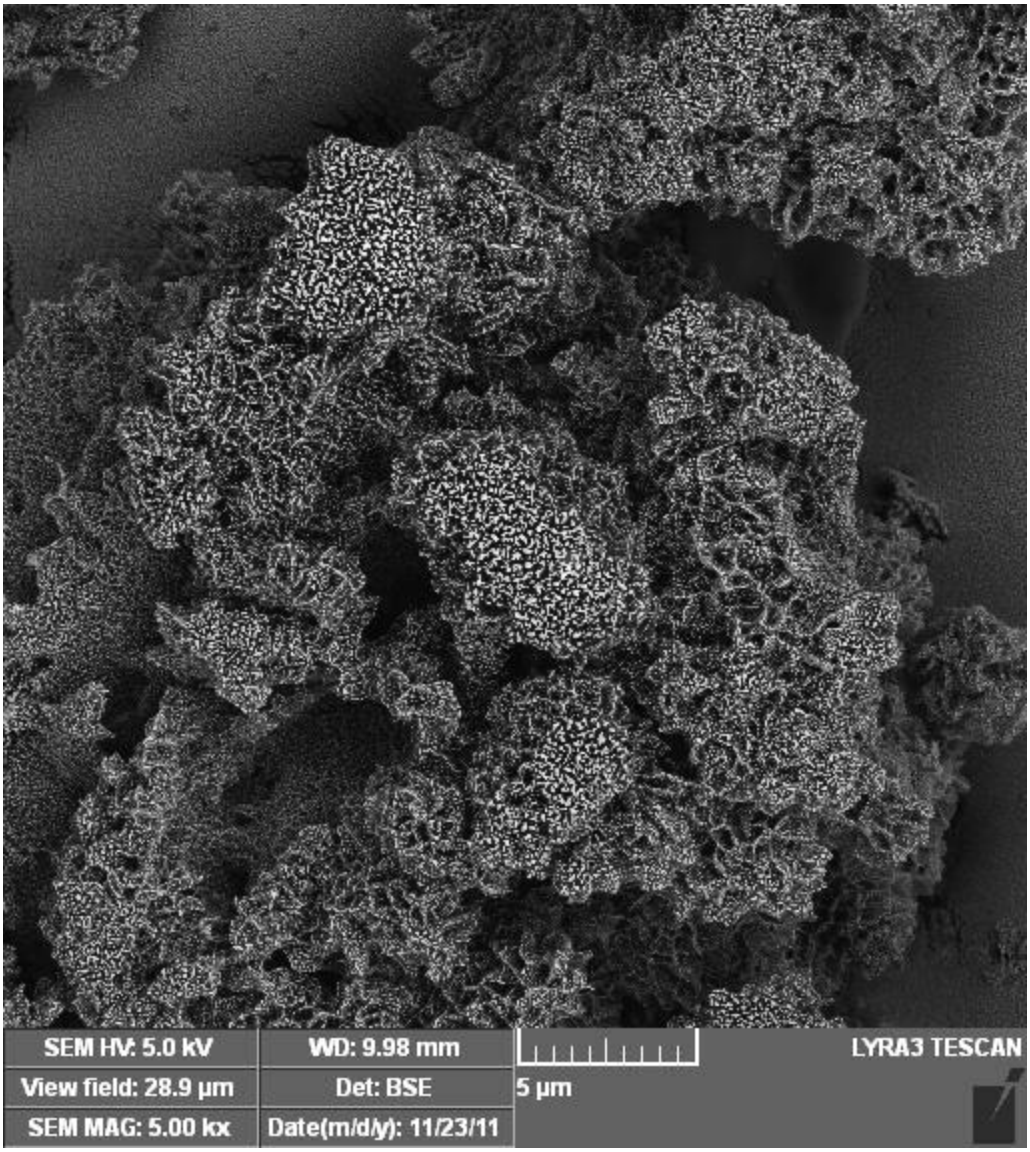

Figure 9 (A-D): Scanning Electron microscopy of nano-AlN filled polyethylene composites C-30mg AlN/ HDPE

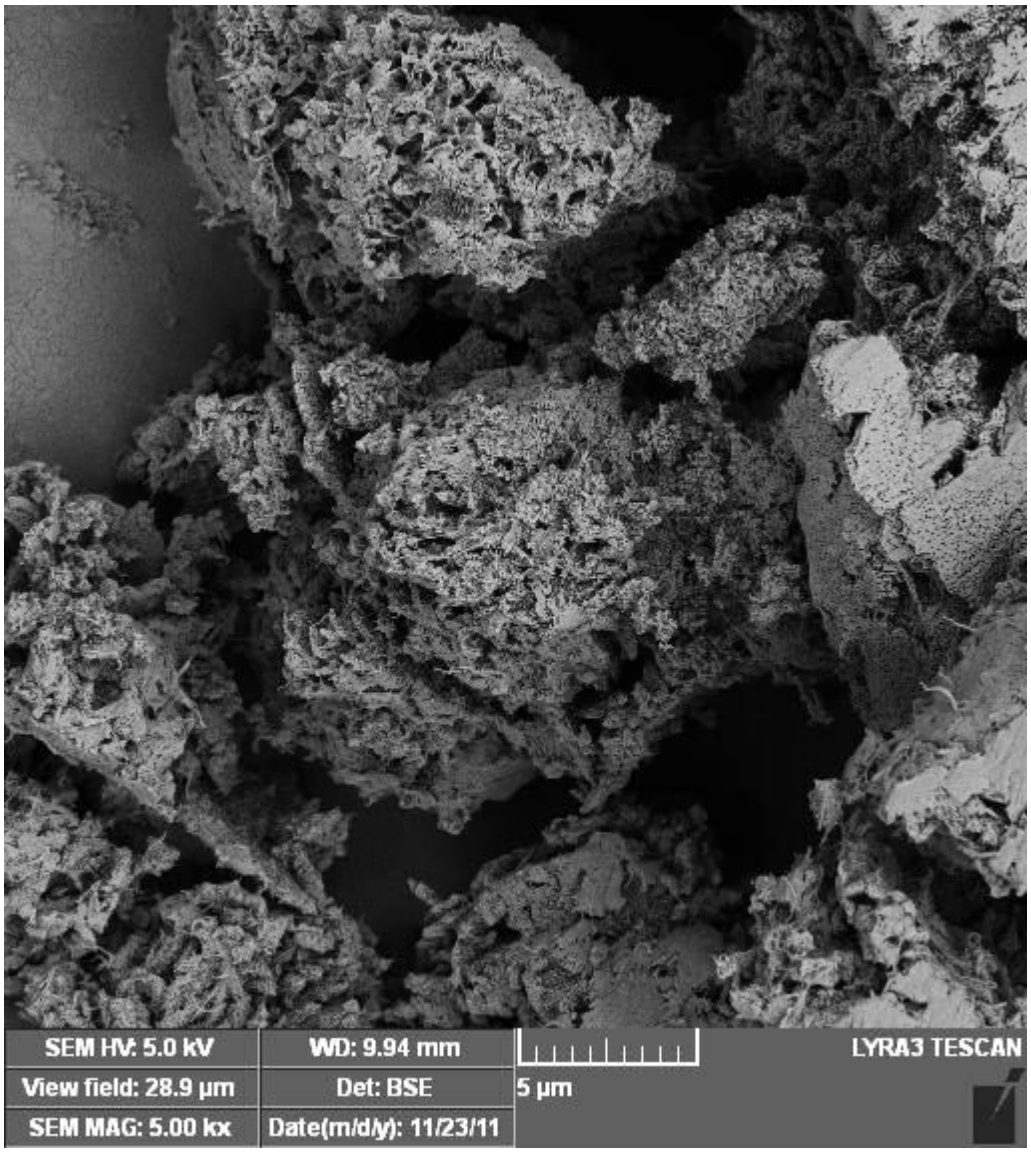

Figure 10 (A-D): Scanning Electron microscopy of nano-AlN filled polyethylene composites D-45mg AlN/ HDPE

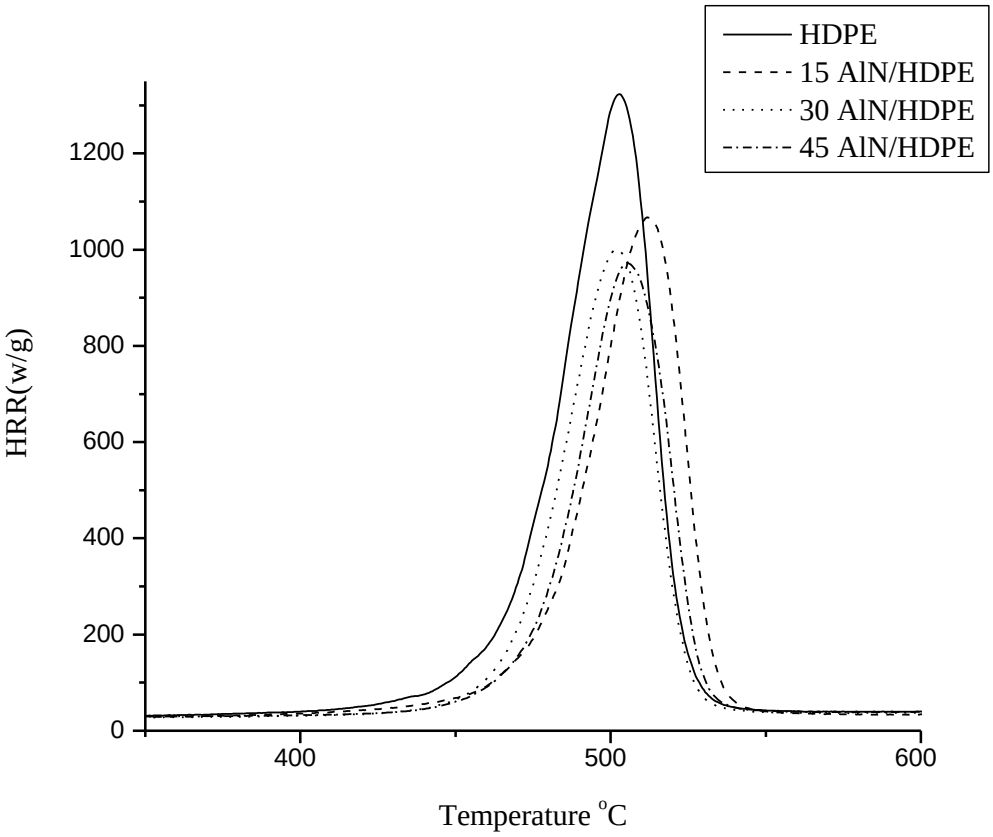

Figure 11 **Heat release rate vs Temperature**

Table 3 Experimental conditions used for the preparation of polyethylene through insitu polymerization by using zirconocene and MAO co-catalyst system

Entry No.	Filler (mg)[a]	Temp (^oC)	Activity[d]
1	0[c]	30	149.46
2	15	30	329.62
3	30	30	189.41
4	45	30	107.01
5	0[c]	60	181.15
6	15	60	235.54
7	0[b,c]	30	132.80
8	15[b]	30	267.67

[a]AlN
[b]with 3 ml MAO
[c]Control
[d] x 10^{-5} gPE/mol Zr h bar

Table 4 DSC and XRD results of AlN filled polyethylene composites

Material	ΔHfus (J/g))	Tm (OC)	Percentage Crystallinity	Percentage Crystallinity
HDPE	207	135	70	66
15 AlN/HDPE	216	133	74	68
30 AlN/HDPE	210	130	71	66
45 AlN/HDPE	201	131	68	65

Table 5 Micro-Calorimeter

Material	Decomposition Temperature (^{o}C)	HRR (W/g)
PE	502.7	1323.2
PE/15 mg AlN	511.8	1067.4
PE/30 mg AlN	501.8	998.7
PE/45 mg AlN	505.6	972.6

CHAPTER 4

EFFECT OF SILICON (SIN) ON THE PROPERTIES OF POLYETHYLENE

Many applications these days requires heat sinks within the polymer matrix, in order to provide a better thermal stable polymers, therefore appropriate fillers must be used [1].Polymer Nanocomposites provide a varied combination that is difficult to achieve by a single component. [2-3].High Mol wt. Polyethylene has various applications in industry because of its high impact strength (HIS), excellent resistency to chemicals and biocompatibility [4].During the development of micro electronics technology in order to provide a smartness in gadgets, usage of physical bulky heat sinks become outdated [5].Many Plastic Materials are used for packaging because of their high electric resistances low dielectric constants and good process abilities. Polymers that are commonly used are polyethylene (PE), is not so good in effective heat dissipation. So to make them effective, fillers are being used that can compete in new market [6].Nano silicon nitrides were used with polypropylene in a twin screw extruder in order to make a mechanical reliable material. [7].

In regard to catalyst activity in polymerization of ethylene, metallocene catalysts provide more flexibility than Ziegler-Natta catalysts. In earlier studies Polyethylene (PE) was synthesized using metallocene catalysts, with the support of zeolite where in methylaluminoxane (MAO) was used then as co-catalysts [8]. Problem still exist in

regard to control the polymer morphology with soluble catalysts and a large amount of MAO needed to achieve maximum catalyst activity [9].There are reports on attempts to use the metallocene catalysts for industrial purposes [10-13].

Organic Polymers are combustible and flame retardants are used to compress the combustible process [14,15].The present reports the result of studies on the properties of polyethylene nano-composites prepared by using metallocene catalysts in presence of silicon nitride.

4.1 Experiments

4.1.1 Material

Silicon Nitride (SiN) having size less than 50 nm, zirconocene (catalyst), Toluene and co-catalyst MAO (methylaluminoxane) were purchased from Aldrich Chemicals and kept in oxygen free environment to avoid any contamination. Ethylene was available in the reactor form cylinder.

4.1.2 Preparation

Polymerization of ethylene was performed in a 250 ml round-bottom flask equipped with a magnetic stirrer. The zirconocene catalyst (6 mg) and required amount of nano-SiN (0, 15, 30 and 45) mg were added to the flask. The reactor was charged with toluene coming from purification chamber so that any of the contamination might not affect the catalysts and co-catalyst. MAO (methylaluminoxane) (5 ml) was used as co-catalysts. The whole process was performed inside a glove box. The reactor was then immersed in a constant

temperature bath previously set to desired temperature (30^{o}C, 60^{o}C). After ensuring that bath temperature and reactor temperature was the same, ethylene was introduced into the reactor through an external chamber after removing nitrogen gas under vacuum. Polymerization was quenched after 30 minutes by adding methanol. The polymer was washed with an excess amount of methanol and dried in an oven at 50^{o}C. The conditions used for these present study is given in Table 1.

4.2 Characterization

4.2.1 Activity

Activity of the catalysts is measured by weighing the product and activity was noted as ratio of amount of product (Polyethylene nanocomposite) to amount of catalyst consumed.

4.2.2 Differential Scanning Calorimeter (DSC)

The melting and crystallization behavior of the composites were determined by using DSC-Q1000 (TA instruments). To overcome the thermal history, heating and cooling was done for both first and second cycle's nitrogen atmosphere at the rate of 10°C/min and 5°C/min respectively from a temperature of -10°C to 200°C and third cycle was performed at a rate of 10°C/min and is analyzed in this study.

4.2.3 X-Ray Diffraction (XRD)

Diffractions patterns were obtained through (Rigaku Ultima IV) and crystallinity was determined [16].

4.2.4 Thermo-Gravimetric Analysis (TGA)

Thermal degradation studies were performed by thermo gravimetric measurements using TGA- Q500 (TA instruments). Samples weighing approximately 5 mg were heated in nitrogen atmosphere (purge gas flow: 50 mL/min) from 25° to 650°C at a heating rate of 10°C/min.

4.2.5 Scattering Electron Microscopy (SEM)

The Polymer surface was gold coated and then surface morphology was studied by using Scanning Electron Microscopy (LYRA3GM, TESCAN).

4.2.6 Micro-Calorimeter (MC)

Heat release rate and ignition temperature was determined by using micro-calorimeter (FAA Micro-calorimeter) and sample size varied from 3-4 mg.

4.3 Result and Discussion

4.3.1 Activity

Figure 1 represents the variation in the activity of synthesized polyethylene under various experimental conditions. It was found that the activity of polymerization reaction was higher for the composites having 15 mg of nano-filler (entry no 2) which were prepared using 5 ml of co-catalyst at 30°C. However, further increase in filler content does not improve the activity of polymerization compared to the control (entry no 3 and 4).This observation is similar to that observed earlier in case of Mn doped –titania on the activity of metallocene catalyst by in-situ ethylene polymerization [17]. In order to verify the

influence of temperature on activity, reaction was conducted at 60^{o}C (entry no 5 and 6). It is clear from the figure that at high temperature (60^{o}C) activity of reaction increased (entry no 6) when compared to control (entry no 5) but lower than the activity obtained for the reaction at 30^{o}C (Table 1). Reduction in the amount of co-catalyst also increased the activity of the reaction and was higher for the composites having 15 wt. % of nano-filler (entry no 7 and 8).

4.3.2 Differential Scanning Calorimeter (DSC) and Xray Diffraction (XRD)

Figure 2 displays thermo graph of polyethylene composites as a function of SiN. Heat of fusion and fusion temperature values along with percentage crystallinity for blends as function of SiN is summarized in Table 2. It can be seen from the DSC results that amount of fillers become increasing function of fusion Temperature [18]. Percentage Crystallinity was calculated using the following expression is shown in table 2

$$\% \text{ of crystallinity} = (\Delta H_{fus}/\Delta H^{0}_{fus}) \times 100 \quad (5)$$

where ΔH_{fus} is the enthalpy of fusion of the polyethylene composites and ΔH^{0}_{fus} is the enthalpy of fusion of 100% crystallinity of polyethylene which was taken as 2935 J/g [19].Slight decrease in crystallinity from 0 mg to 15mg is due to proper dispersion, disturbed the crystallinity of polymer matrix [20-23].And then with increase in the filler loading, decrease in crystallinity is attributed to the heterogeneous nature imparted by the nano-fillers which results in an increase in the crystallinity of the composites [24]. Crystallinity is determined through x-ray diffraction (Rigaku Ultima IV), and it showed the same trend as from DSC results as shown by figure 2 (b) [16, 25].

4.3.3 Thermal Gravimetric Analysis (TGA)

Figure 3 and 4 displays TG and DTG curves for PE composites as the function of amount of filler. From the TG curves it is clear that degeradation starts at 350^{o}C and of 45 mg SiN/HDPE its observed maximum at temperature of 450^{o}C.

The degradation kinetics of the composites can be calculated by using Broido method [26]. based on the assumption that the degradation follows a first order reaction or a superposition of first order process. This assumption of Broido leads to:

$$\ln[-\ln(1-\alpha)] = \ln \mathrm{K} - \frac{\Delta E}{RT} \tag{3}$$

Where α the amount of polymer degraded at time t**,** ΔE is the change in activation energy, R is the universal gas constant and T is the temperature in Kelvin scale and K is apparent activation energy. In this, α can be calculated using the following equation:

$$\alpha = \frac{W_o - W_t}{W_0 - W_\infty} \tag{4}$$

where W_t is the mass at time t, W_o is the initial mass and W_∞ is the mass after infinite time. The advantage of Broido's method of calculating the activation energy of thermal stability is that the result does not depend upon the value of heating rate and is independent of the value of temperature at which the reaction is maximum. The results obtained by using Broido's method for the SiN/Polyethylene composites are given in Figure 4. It can be seen that composites having 15 mg of SiN shows maximum activation energy as compared to other compositions.

4.3.4 Micro-Calorimeter (MC)

Combustibility test data as obtained through Micro Calorimeter in terms of heat release rate and decomposition temperature are shown in table 3, it is apparent that with increase in the content of filler, heat release rate decreases indicating an increasing in thermal stability and decrease in combustibility [15].

4.3.5 Scanning Electron Microscopy (SEM)

Fig (6a-6d) shows surface morphology, HDPE appears to be less fibrous (see fig 6a) than HDPE/15 mg SiN and HDPE/30mg SiN(see fig 6b and Fig 6c).Here fibrous chains are formed making the material more crystalline. In PE/45 mg SiN fibrous surfaces became least prominent (see fig 6d). Scanning Electron Microscopy (SEM) provided us an advantage of exploring the surface morphology of PE (pure) and PE/SiN composites in a better way and same type of effect is also observed in previous studies [27,28].

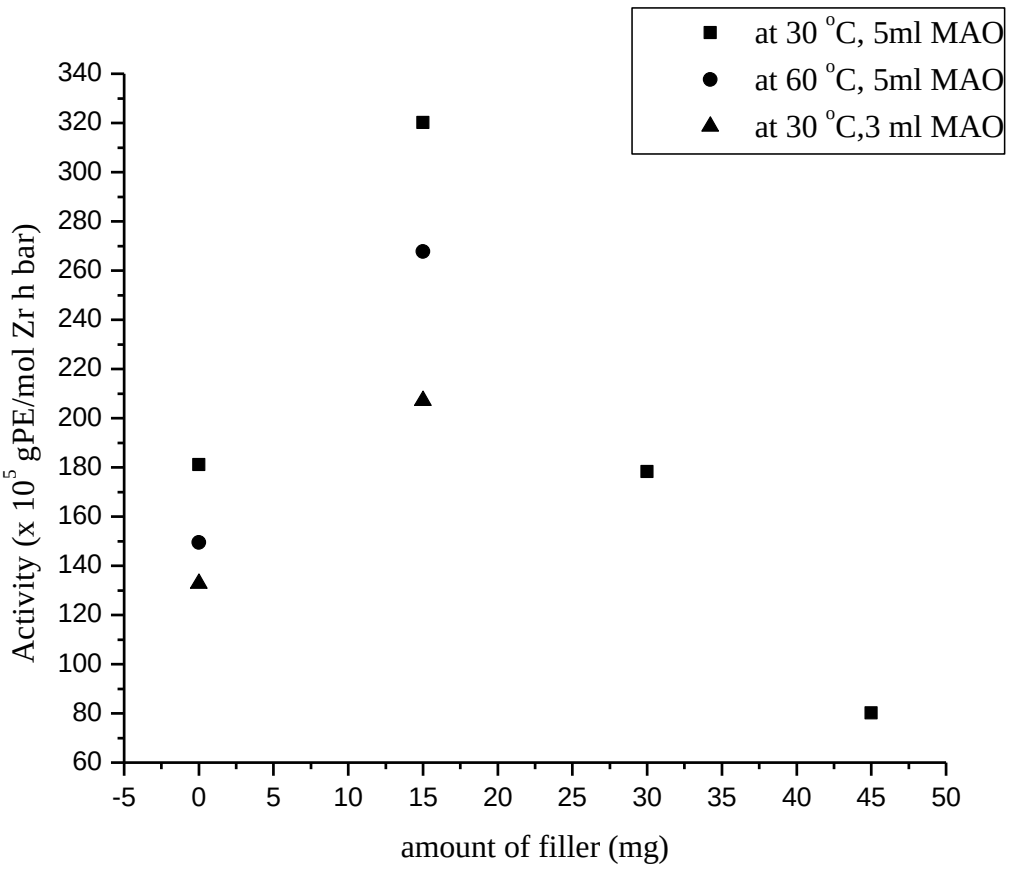

Figure 12 **Activity of synthesized polyethylene nanocomposites at different experimental conditions**

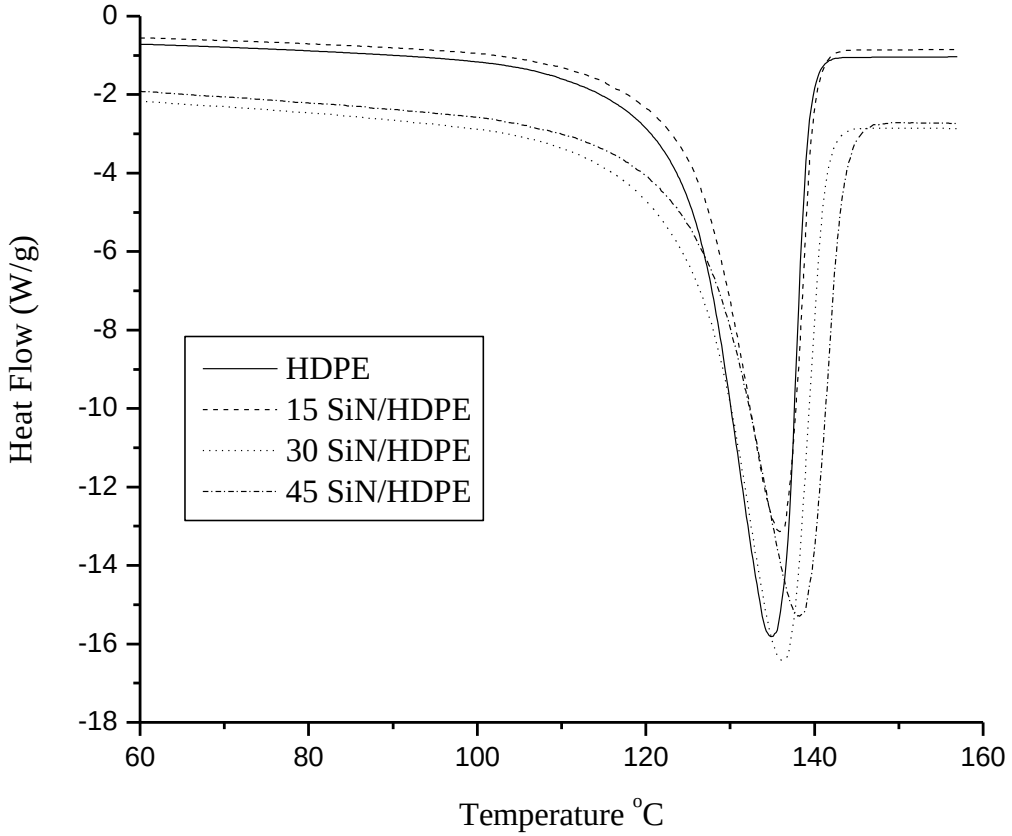

Figure 13 **DSC heating curves of nano-SiN filled polyethylene composites**

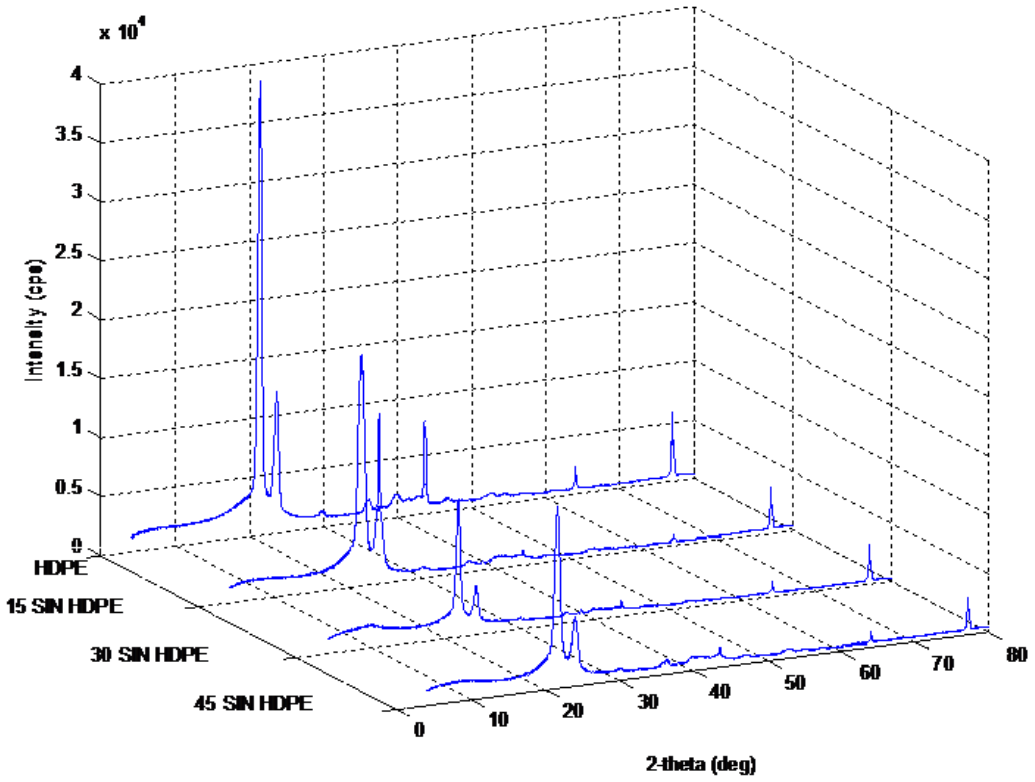

Figure 14 **Xray Diffraction (XRD)-intensity vs 2-theta (deg)**

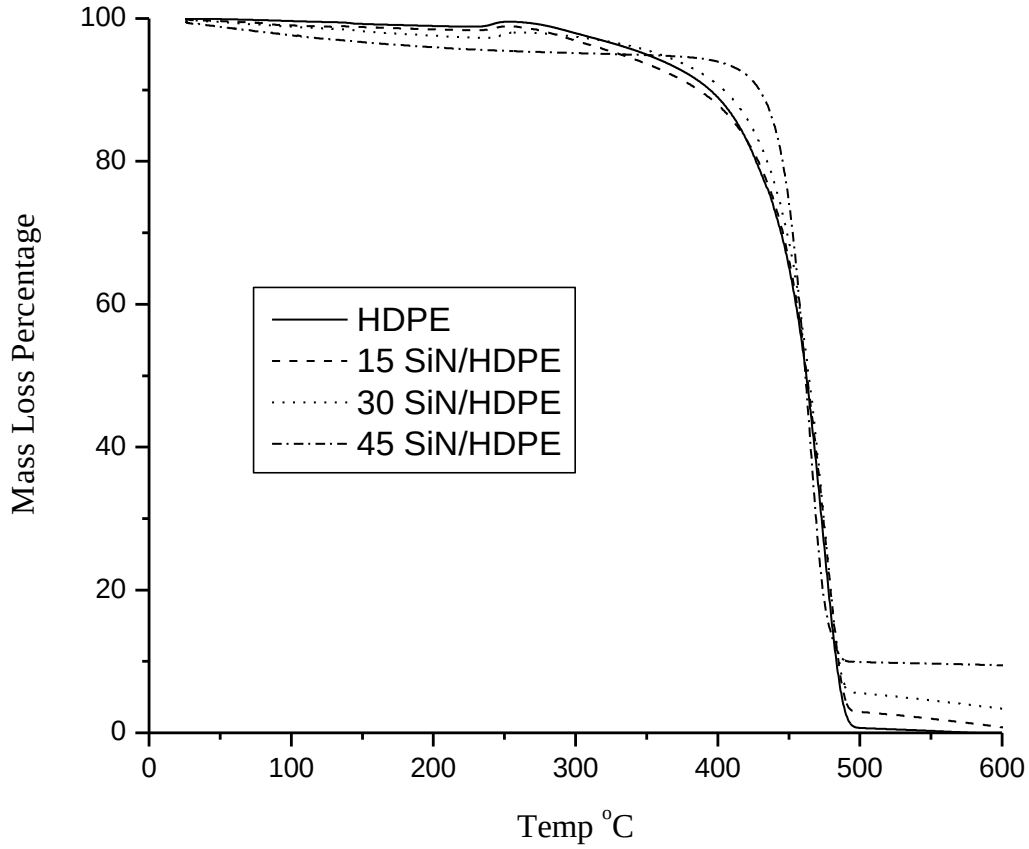

Figure 15 **TG plots of nano-SIN filled polyethylene composites**

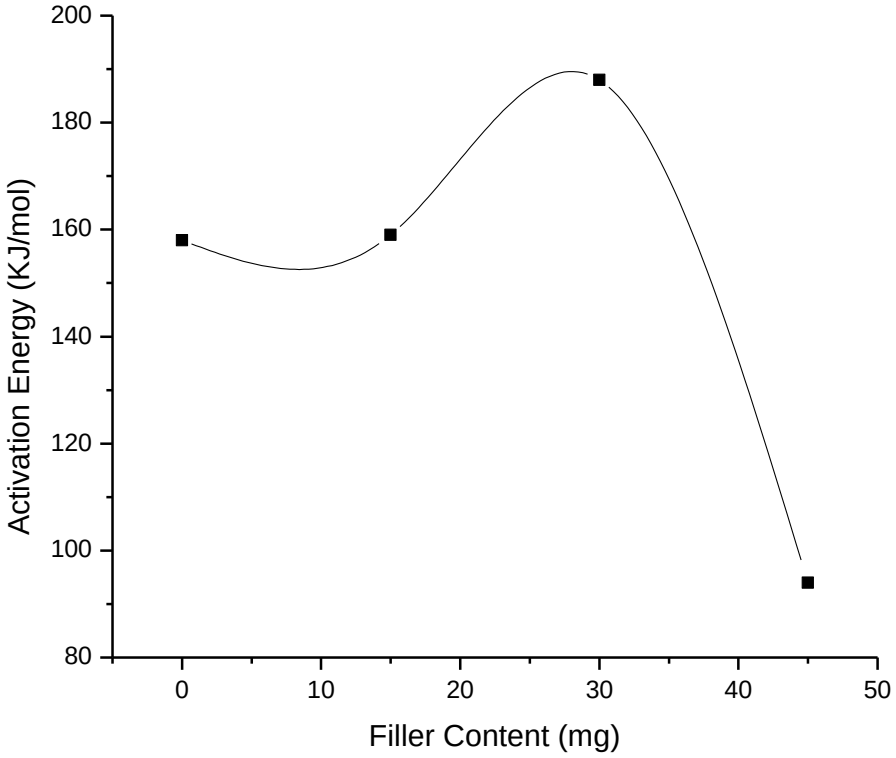

Figure 16 **Change in activation energy for the AlN/Polyethylene composites**

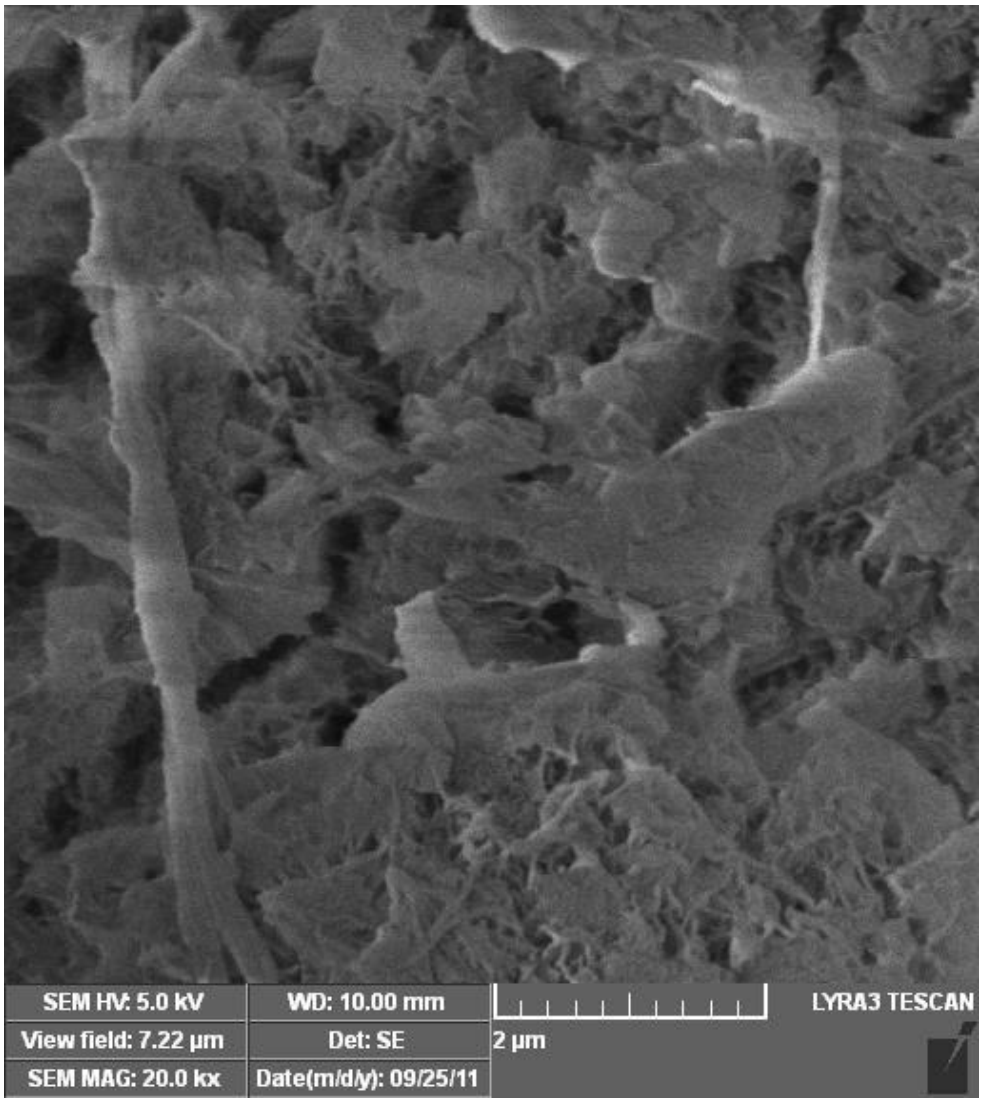

Figure 17 (A-D): Scanning Electron microscopy of nano-SIN filled polyethylene composites A-Pure HDPE

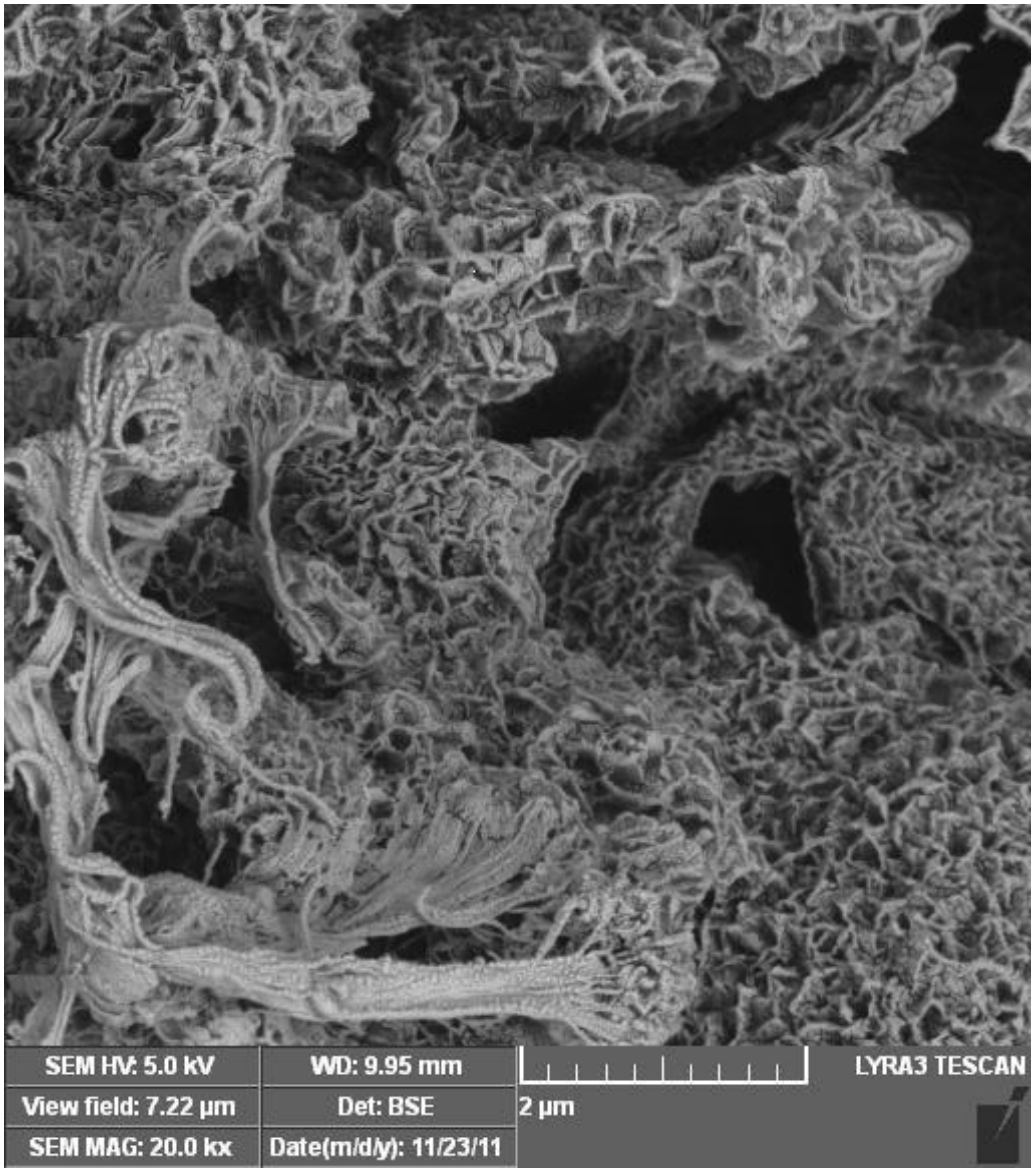

Figure 18 **(A-D): Scanning Electron microscopy of nano-SIN filled polyethylene composites B-15mg SIN/ HDPE**

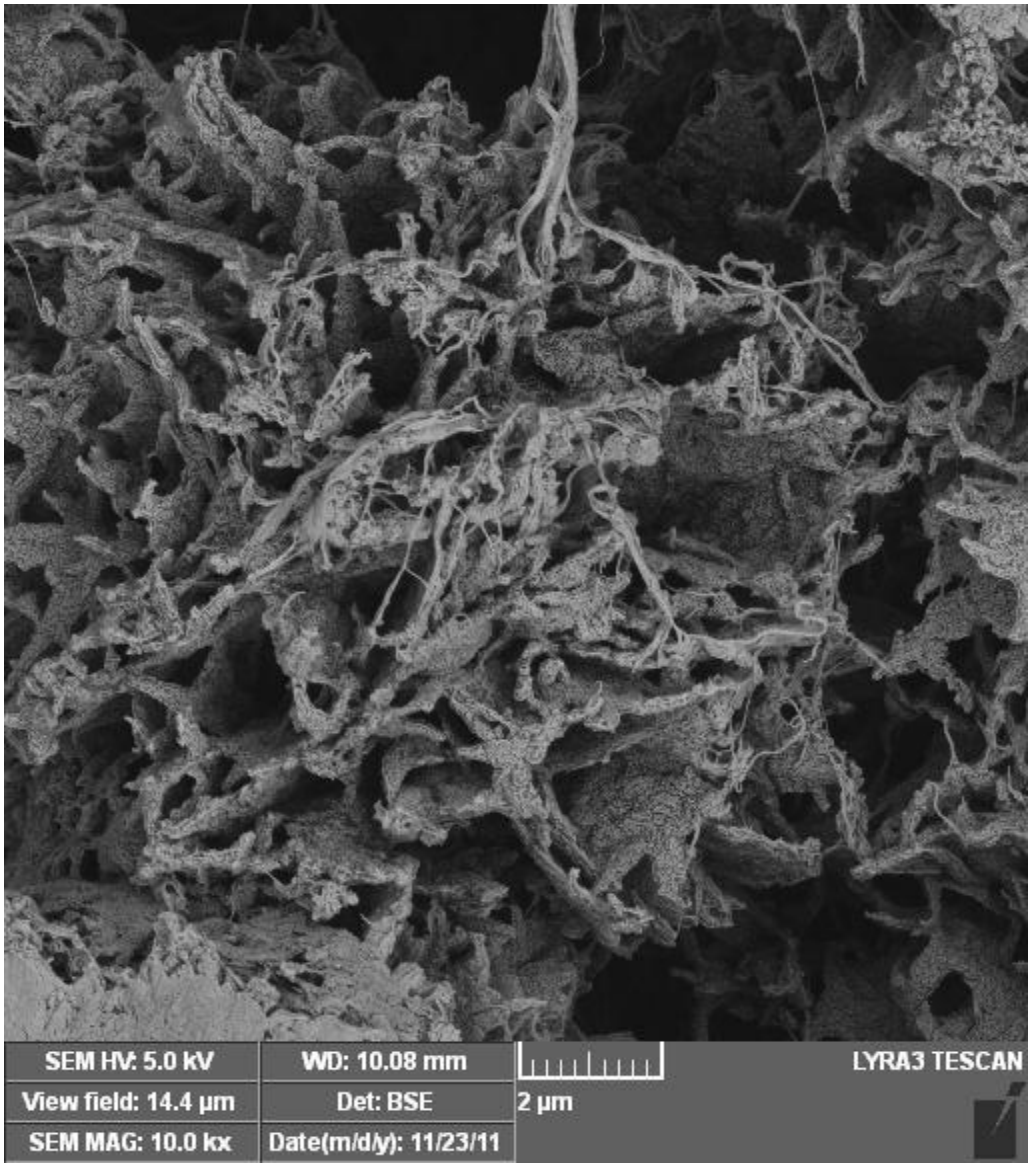

Figure 19 **(A-D): Scanning Electron microscopy of nano-SIN filled polyethylene composites C-30mg SIN/ HDPE**

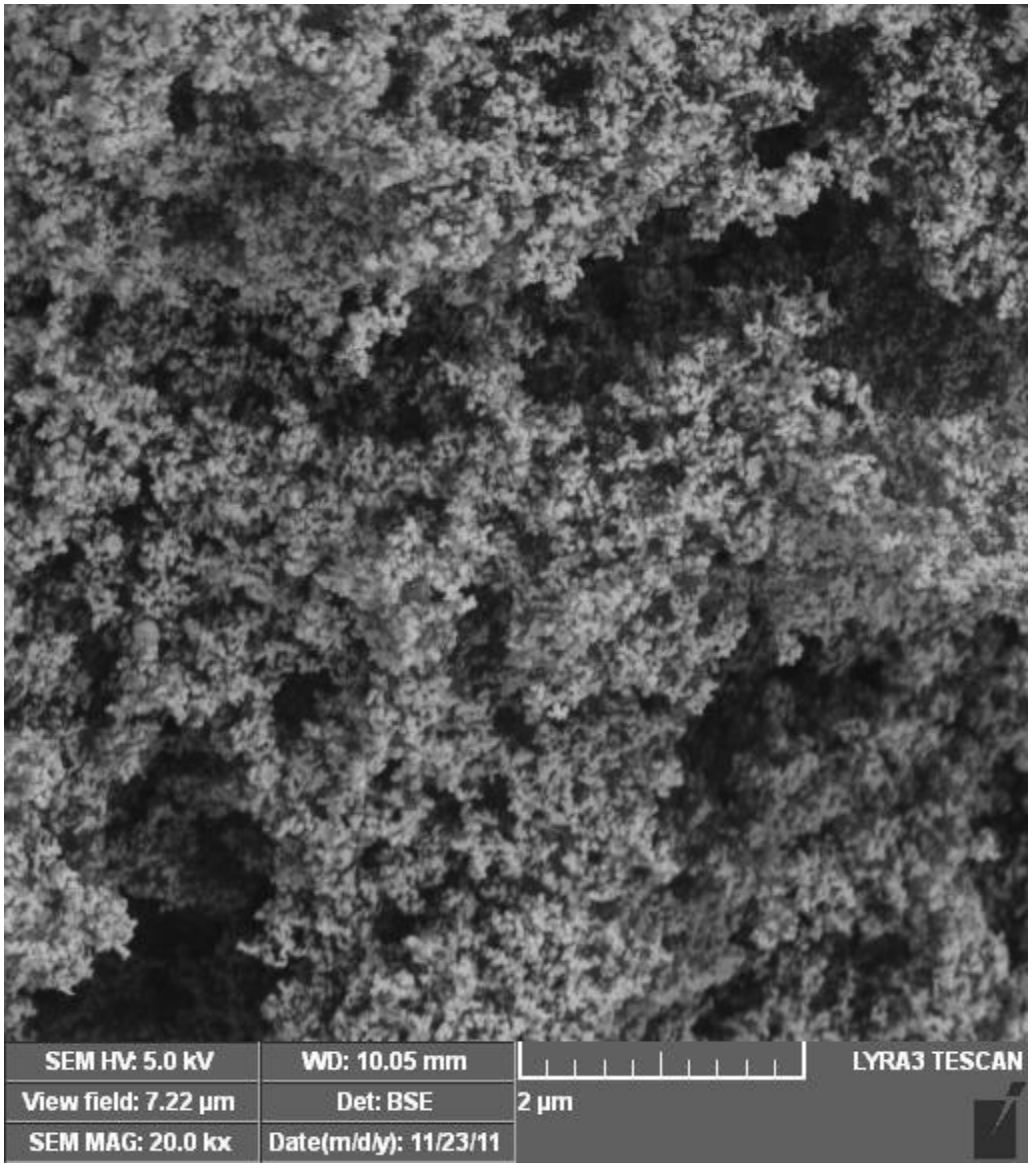

Figure 20 (A-D): Scanning Electron microscopy of nano-SIN filled polyethylene composites D-45mg SIN/ HDPE

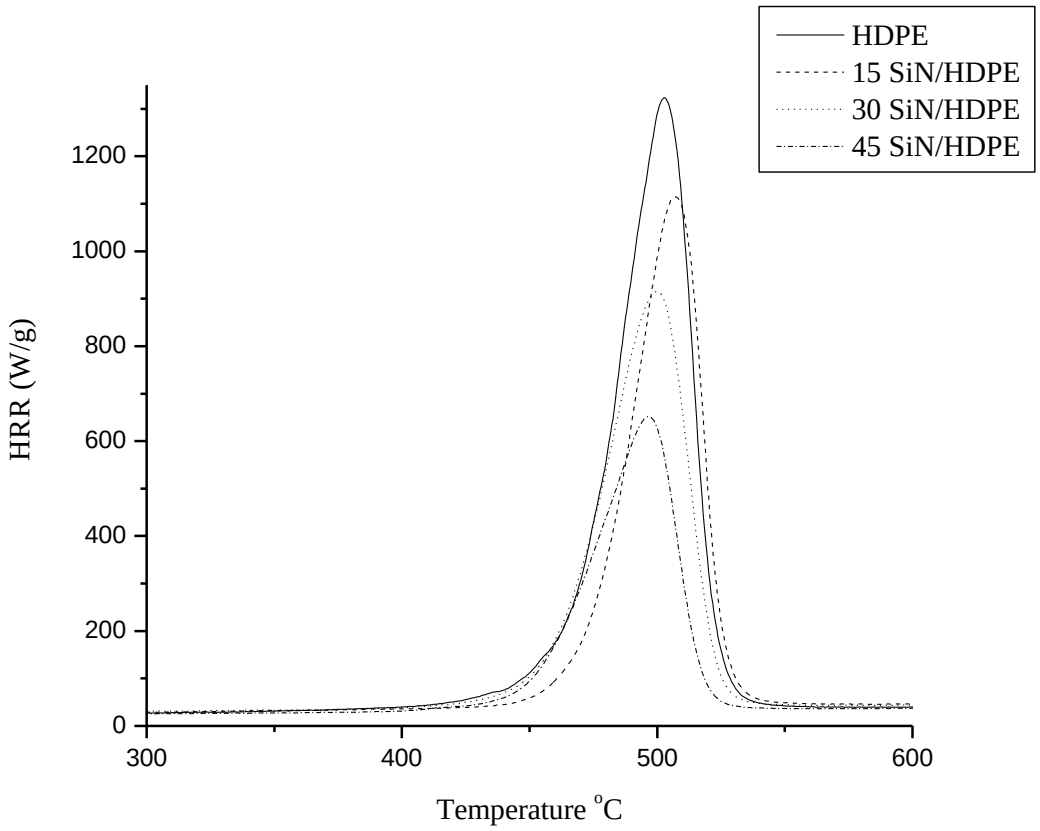

Figure 21 **Heat release rate vs Temperature**

Table 6 Experimental conditions used for the preparation of polyethylene through insitu polymerization by using zirconocene and MAO co-catalyst system

Entry No.	Filler (mg)[a]	Temp (^oC)	Activity[d]
1	0[c]	30	181.15
2	15	30	320.17
3	30	30	178.22
4	45	30	80.12
5	0[c]	60	149.46
6	15	60	267.67
7	0[b,c]	30	132.80
8	15[b]	30	207.13

[a]SiN
[b]with 3 ml MAO
[c]Control
[d] x 10^{-5} gPE/mol Zr h bar

Table 7 DSC and XRD results of SIN filled polyethylene composites

Material	ΔH_{fus} (J/g))	T_m (^OC)	Percentage Crystallinity (DSC)	Percentage Crystallinity (XRD)
HDPE	207	135	70	66
15 SiN/HDPE	216	136	54	50
30 SiN/HDPE	210	136	63	58
45 SiN/HDPE	201	138	58	53

Table 8 Micro-Calorimeter

Material	Decomposition Temperature (^{o}C)	HRR (W/g)
PE	502.7	1323.2
PE/15 mg SiN	507.0	1114.8
PE/30 mg SiN	500.0	915.2
PE/45 mg SiN	552.7	652.0

CHAPTER 5

EFFECT OF CERAMIC NANO-FILLER ALUMINUM NITRIDE ON MECHANICAL AND THERMAL PROPERTIES OF LDPE

Polymers gain importance because of their wide range of application, low cost, low density, durability and mechinability [1].Among thermoplastic polymer LDPE is of more technological interest because it can be easily processed and is non-polar semi crystalline. In addition to that, production of nanocomposite based on LDPE could improve the mechanical and thermal properties [2].

Many applications in present situation requires thermal conductive polymer materials, therefore many thermal conductive inorganic fillers are filled with polymers to overcome thermal management issues effectively [3-5].In concern with thermoplastic matrices, addition of filler also improves mechanical properties such as Young's Modulus [6].Some studies discussed improvement of physio-mechanical properties of LDPE by the addition of inorganic nano fillers [7].In one of the study addition of nano-silica particles increased the elastic modulus and tensile strength of LDPE dramatically [8].

Recently different kinds of Polymer Nanocomposites are studied actively on the dielectric properties [9]. .In one of the study superiority of dielectric properties of LDPE/MgO nano composites over micro composites was also studied [10, 11].

Aim of this study is to investigate the effect of various loadings of nano-AlN on mechanical, dielectric and thermal behaviour of LDPE.

5.1 Experiments

5.1.1 Material

LDPE with density of 0.92 g/cm^3 was purchased from Exxon Mobil Chemicals, Belgium (Mw=92740, MFI=2 g/10 min). Aluminum Nitride (AlN) nano-powder of size less than 100nm particle size was obtained from Sigma Aldrich.

5.1.2 Preparation

LDPE was blended with AlN, in the ratio of 100/0, 100/0.25, 100/0.50,100/1 by weight in a Brabender Plasticorder (Mixer 50E) at 140^{o}C for 10 minutes and blends are designed as 0.25 AlN/LDPE, 0.50 AlN/LDPE and 1.0 AlN/LDPE respectively. Mixer Speed was kept at 60rpm.The blend was compressed in carver press at 140^{o}C for 5-7 minutes to prepare sheets of thickness approx. 2mm.

5.2 Characterization

5.2.1 Mechanical Testing Analysis

Tensile properties of the dumbbell-shaped were measured at 25^{o}C as per ASTM D638 using Instron UTM (Model 5560) at the crosshead speed of 50mm/min.

5.2.2 DSC analysis

The melting and crystallization behavior of LDPE and LDPE/AlN-nano composites were determined by using DSC-Q1000, Universal V4.2E TA instruments. First cycle (Heating) and second cycle (Cooling) were done in nitrogen atmosphere at the rate of 10^{o}C/min from 20^{o}C-180^{o}C.The crystallanity of LDPE and the blends was calculated by using the expression.

$$\% \text{ of crystallanity} = (\Delta H_{fus}/\Delta H^{0}_{fus}) \times 100$$

ΔH_{fus} is the enthalpy of fusion of LDPE/AlN nano composite. ΔH^{o}_{fus} is the enthalpy of fusion of 100 percent crystalline LDPE. Delta H fusion of LDPE was taken as 295 J/g

5.2.3 Rheological Analysis

Rheological measurements were done with the help of advance rheometric expansion system (ARES). These measurements were performed by using cone and plate geometry (25 mm dia., 0.1 radian cone angle and 0.4554 mm gap) at 150^{o}C in N_2 environment. Angular velocity of 0.1-100 rad/s with linear visco-elastic regime at a strain of 10% was applied.

5.2.4 Dielectric Properties

DC volume resistivity was of the nano composites were measured using Agilent 4339B (High resistance meter attached with Agilent 16008B, resistance cell.

5.2.5 Micro-calorimeter

FTT micro-calorimeter was used to measure Specific Heat Release Rate (W/g) vs. Temperature (^{o}C) of LDPE and LDPE/AlN-nano composites. FTT micro-calorimeter is accurate and cost effective calorimeter using a technique of Pyrolysis Combustion Flow Calorimeter (PCFC).

5.3 Results and Discussion

5.3.1 Mechanical Testing Analysis

Tensile strength and modulus values of LDPE and LDPE/AlN-nano composites are shown in Table 1. Modulus decreases with the increase in filler loading. This effect is due to agglomeration of nano filler in polymer matrix and same phenomenon is also observed in other studies [12, 13].

5.3.2 DSC Analysis

DSC curves for LDPE and LDPE/AlN-nano composites are shown in Figure 1, percentage crystallanity and melting temperature is also tabulated in Table 2. With increase in the filler loading, percentage crystallanity decreases with marginal effect on melting temperature. An effect of decrease in crystallanity is due to the disturbance and disorientation of chains due to fillers, accommodated in polymer matrix. Other literature studies also show same type of effect [14, 15].

5.3.3 Rheology

Figure 2 and Figure 3 shows Storage Modulus (G') and loss Modulus (G'') as a function of frequency for LDPE and LDPE/AlN-nano composites respectively. These results show that LDPE/AlN-nano composites with diff wt % filler loading show same trends and are superimposed. Same Phenomenon is observed in another study [16]. Presence of AlN increased the storage modulus and loss modulus when compared to neat LDPE. But as the frequency increases elastic modulus of all the composition including neat LDPE superimposed because of provision of insufficient relaxing time of polymer chains.

Figure 4 shows Tan δ as a function of frequency for LDPE and LDPE/AlN-nano composites. Tan δ of neat LDPE decreased with the addition of AlN, both at lower and higher frequency range. Dynamic storage modulus (G') at lower frequency regime generally shows same kind of trend as because when polymer reinforced with nano-fillers improve the viscoelastic property [17-18].

Since nano fillers exhibits large surface area so they have ability to produce an effect of particle-polymer or particle-particle thermodynamic interactions, when particle-particle interaction dominates, as can be believed at higher frequency than rheological response can be believed on destruction and reconstruction of particle network[19]. However when particle-polymer network dominates, as can be considered at lower frequency, then rheological response is controlled by dynamics of the stick-slip motion of polymer chains around the particle surface [20].

5.3.4 Dielectric Properties

Figure 6 shows Log (DC) as a function of Log (F). With increase in the filler loading DC decreases at both low and high frequency. Phenomenon that best describes this situation is, nano fillers in the polymer constitute a connection between them and intrinsic dipoles of host material by Van Der Waals forces restrains the rotation of intrinsic dipoles and molecular chain of polymers when a external electric field is applied and therefore it decreases the polarization intensity which results in negative effect on dielectric constant [21, 22].

5.3.5 Micro-Calorimeter

Figure 7 shows that with increase in the filler loading, Heat Release Rate (W/g) is decreasing without affecting an ignition temperature. Other studies also show that with an increase in amount of filler especially nano-fillers heat release rate of polymer lowers down [23, 24].

If we plot a graph in order to normalize an amount of filler present in a specific quantity of polymer as shown in Figure 8, it shows that there exist an interaction within a filler and polymer matrix that keeps lowering down Heat Release Rate (W/g) violating a linear fashion.

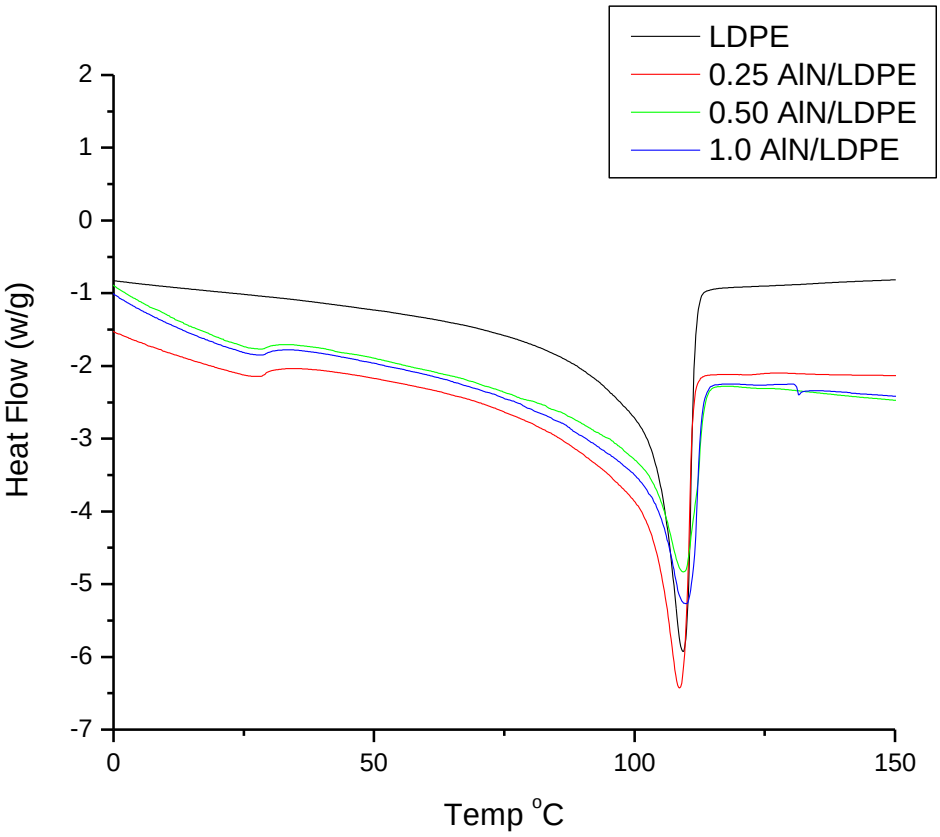

Figure 22 **DSC heating curves of LDPE and LDPE/AlN-nano composites**

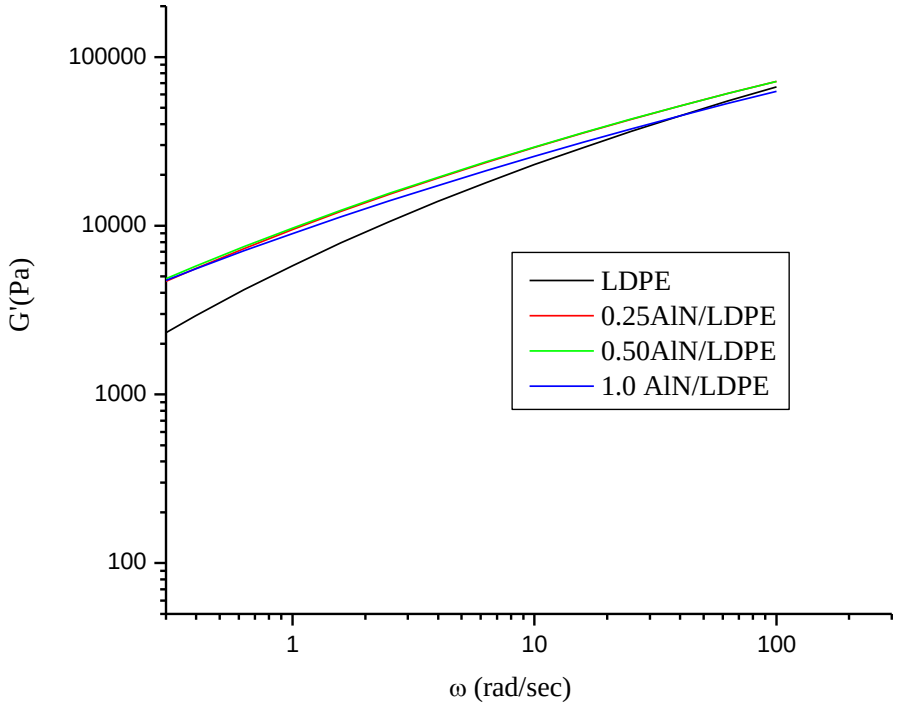

Figure 23Variation in the G' for LDPE and LDPE/AlN nanocomposites as a function of frequency at 150°C

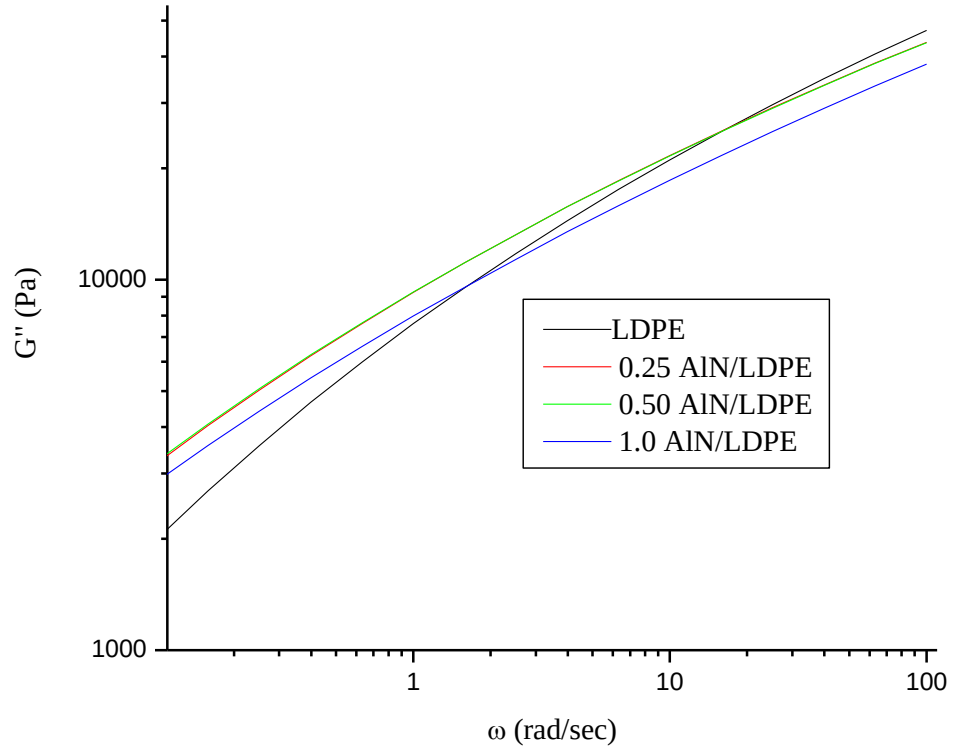

Figure 24Variation in the G' for LDPE and LDPE/AlN nanocomposites as a function of frequency at 150°C

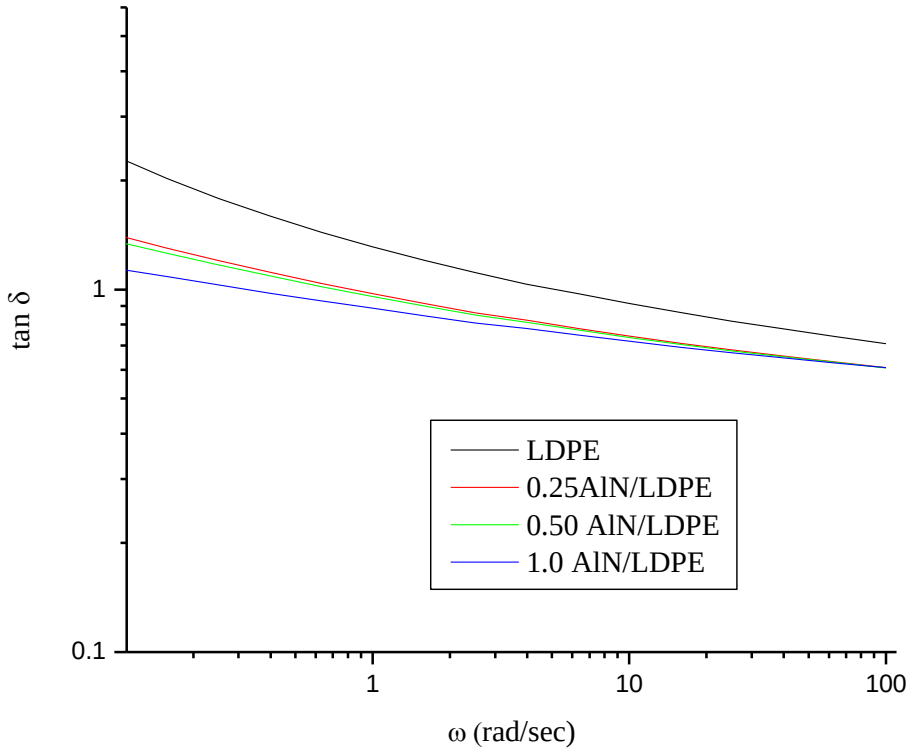

Figure 25Variation in the tan δ for LDPE and LDPE/AlN nanocomposites as a function of frequency at 150°C

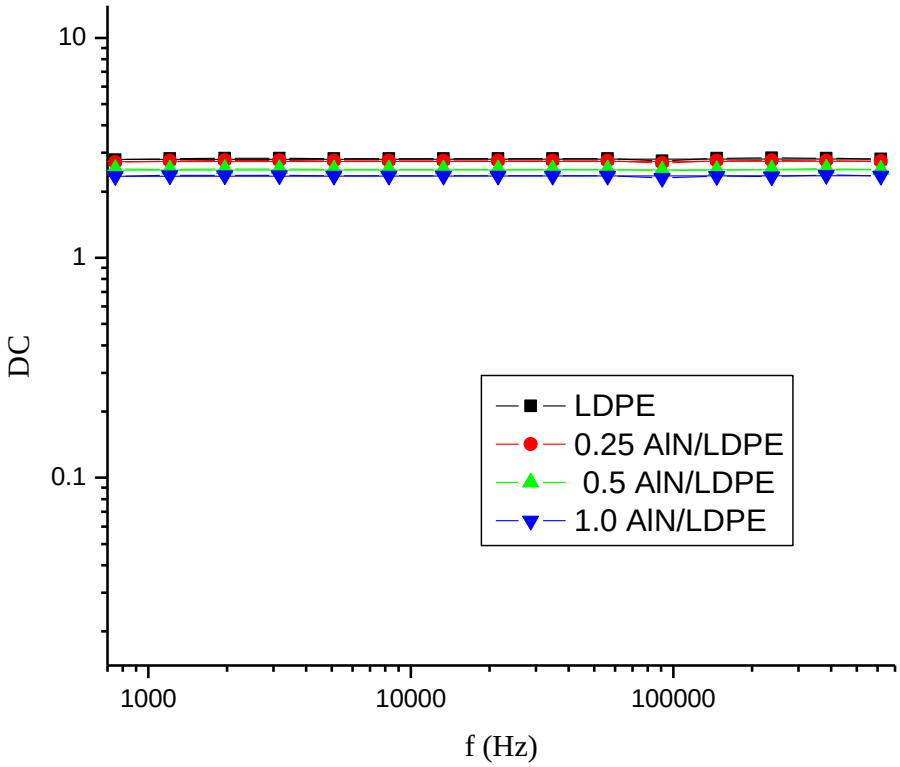

Figure 26 **Dielectric Constant of LDPE and LDPE/AlN nano-composites DC vs Frequency (Hz)**

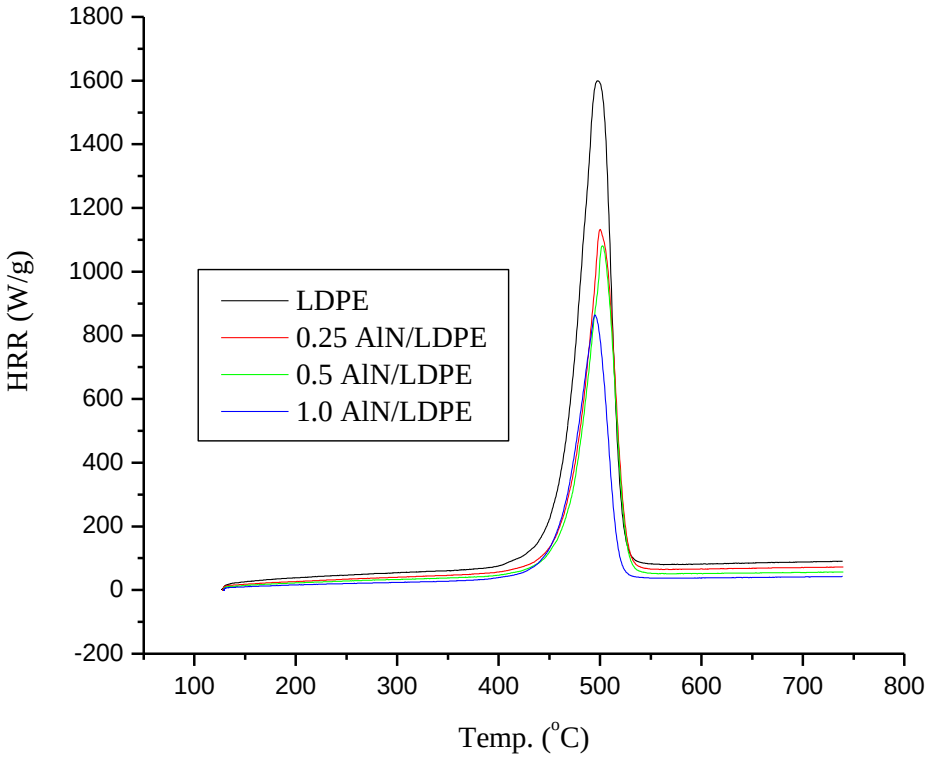

Figure 27 **Heat Release Rate(HRR) vs Temperature (°C)**

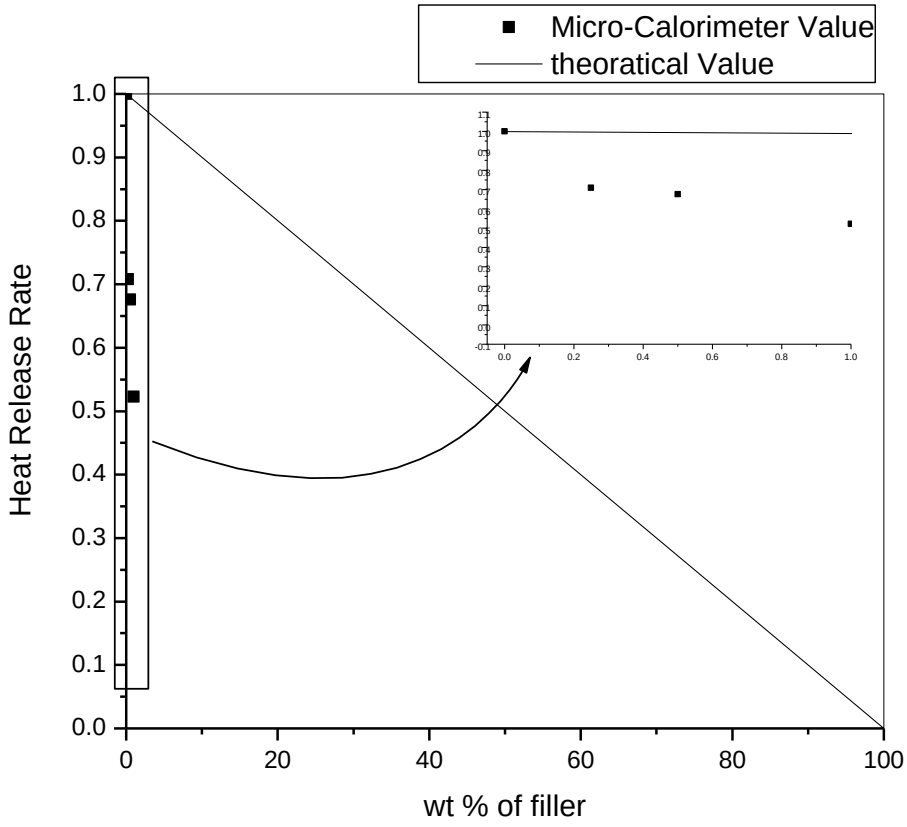

Figure 28 Heat release rate (W/g) vs. amount of filler (normalized weight percent) of LDPE and LDPE/AlN- nano composites

Table 9 DSC results showing Percentage crystallanity and melting temperature.

Material	Heat of Fusion (ΔH_f)	T_m	Crystallanity
LDPE	110.1	109.3	38.2
0.25AlN/LDPE	106.2	108.6	36.2
0.5AlN/LDPE	94.2	109.1	31.9
1.0AlN/LDPE	80.11	109.8	27.3

Table 10 Mechanical Testing results (Stress, Strain and Modulus) LDPE and LDPE/AlN nanocomposites.

Material	Stress	Strain	Modulus
LDPE	15.3	338	210
0.25 AlN/LDPE	13.8	414	204
0.50 AlN/LDPE	14.4	166	201
1.0 AlN/LDPE	12.9	380	165

CHAPTER 6

CONCLUSION

Ethylene Polymerization was done to form polyethylene nano-composites with nano-Aluminum Nitride (AlN) and nano Silicon Nitride (SiN).Catalyst activity was higher at 15 mg nano-aluminum nitride (AlN) nano Silicon Nitride (SiN). Differential Scanning Calorimeter (DSC) results shows that melting temperature is minutely effected with an increase in amount of filler in in both the cases. Whereas Percentage crystallanity data from Differential Scanning Calorimeter (DSC) and X ray Diffraction (XRD) shows that at 15 mg AlN/percentage crystallanity increased marginally. In case of SiN (Silicon Nitride), Differential Scanning Calorimeter (DSC) and X ray Diffraction (XRD) shows a decreasing trend accept at 30 mg SiN/HDPE. It is also apparent from Micro calorimeter (MC) data that with increase in the content of filler, heat release rate decreases, indicating a decrease in combustibility in both cases. Surface morphology was observed through scanning electron microscopy (SEM), at 15 mg AlN/HDPE fibrous chain were formed where as at 30 mg AlN/HDPE and 45 mg AlN/HDPE it became less prominent. In case of SiN (Silicon Nitride) scanning electron microscopy (SEM), at 15 mg SiN/HDPE and 30 mg SiN/HDPE fibrous chain were formed.

In blended samples thermal stability was observed through Differential Scanning Calorimeter (DSC) and it was really interesting to note that with increase in amount of filler, 1 wt% loading trend starts lowering where as at 3% due to ineffective dispersion heating value increases. In SiN/LDPE heating value decreased towards higher filler loading.

In micro-calorimeter pure LDPE has higher heat release rate than consecutive loadings of LDPE/AlN where as in case of SiN (Silicon Nitride) the difference of

HRR (Heat Release Rate) of each additional loading is more obvious than in case of AlN/LDPE different wt% loadings.

In short we can say that with the addition of ceramic nano fillers within the polymer matrix increase thermal stability

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